REACTIONS OF CONJUGATED DIENES CATALYSED BY TRANSITION - METAL COMPLEXES

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ABSTRACT

With the aim of dimerising isoprene in a head-to-tail manner to yield monoterpenoid compounds, its homogeneous reactions with palladium, nickel and rhodium complexes were studied.

Using various palladium-phosphine complexes as catalysts, isoprene was telomerised in high conversions with phenol, alcohols (methanol, ethanol and n-propanol) and (less efficiently) water, yielding linear $C_{10}H_{16}$ dimers and ethers and alcohols of the type $ROC_{10}H_{17}$ (R = Ph, Me, Et, n-Pr, H). Telomerisation with phenol generally yielded ethers of the head-to-head type as the major product, but by variation of triphenylphosphine ligand concentration the tail-to-head ether was instead obtained. In contrast, telomerisation with methanol yielded either the tail-to-tail or the tail-to-head ether as major product, depending on the nature of the phosphine ligand and the reaction temperature. In no case, however, did the amount of the desired head-to-tail ethers exceed 7% of the product.

Nickel-complex catalysts gave considerably lower conversions of isoprene, predominantly to triene dimers. As in the case of palladium the use of different phosphine and phosphite ligands produced some variation in the isomer distribution of the product. These reactions were less selective than the palladium-catalysed reactions; the amount of head-to-tail dimers obtained was higher, reaching 20% in the case of the catalyst system $Ni(CH_2{=}CH\,CN)_2 - P(OEt)_3$.

The reaction of isoprene with rhodium chloride in methanol gave a linear head-to-head dimer LI selectively, but in small conversions. Substituted phenols were selectively produced when isoprene or butadiene was reacted with phenol in the presence of a $RhCl(PPh_3)_3$-NaOPh catalyst; this is in contradiction to a previous claim that phenyl-diene-dimer ethers were obtained.

I have yet to see any problem, however complicated, which when you looked at it the right way did not become still more complicated.

Poul Anderson

ACKNOWLEDGEMENTS

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Finally, thanks to Mrs. Ina Godwin who so ably typed this thesis and drew the figures.

I dedicate this thesis to my parents.

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CHAPTER VI

LIST OF ABBREVIATIONS

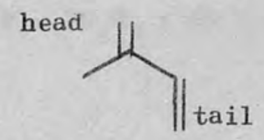
AN	acrylonitrile
ATP	adenosine triphosphate
CTD	1,5,9-cyclododecatriene
COD	1,5-cyclooctadiene
dipy	2,2′-dipyridyl
DVCB	1,2-divinylcyclobutane
MAA	maleic acid anhydride
MHT	3-methyl-1,trans-4,6-heptatriene
OT	1,3,7-octatriene
PBu$_3$	tri-^{n}-butylphosphine
Pcy$_3$	tricyclohexylphosphine
PPh$_3$	triphenylphosphine
THF	tetrahydrofuran
VCH	vinylcyclohexene
VMCP	vinylcyclopentane

CHAPTER I

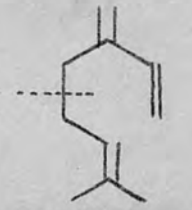
INTRODUCTION

Much effort has been devoted this century to attempts to synthesise terpenoid hydrocarbons from isoprene. The reasons for this are the growing demand for essential oils as flavouring and perfumery agents, and an anticipated increasing difficulty in meeting this demand from natural sources. In addition, isoprene is readily available at a competitive price, because of its use in cis-polyisoprene (synthetic rubber) manufacture(1).

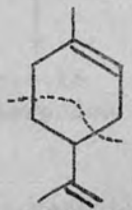
Normally, naturally occurring terpenoids have structures based on C_5 isoprene units linked together in a head-to-tail manner



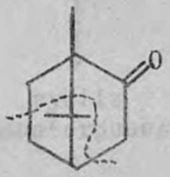
ISOPRENE



MYRCENE



LIMONENE



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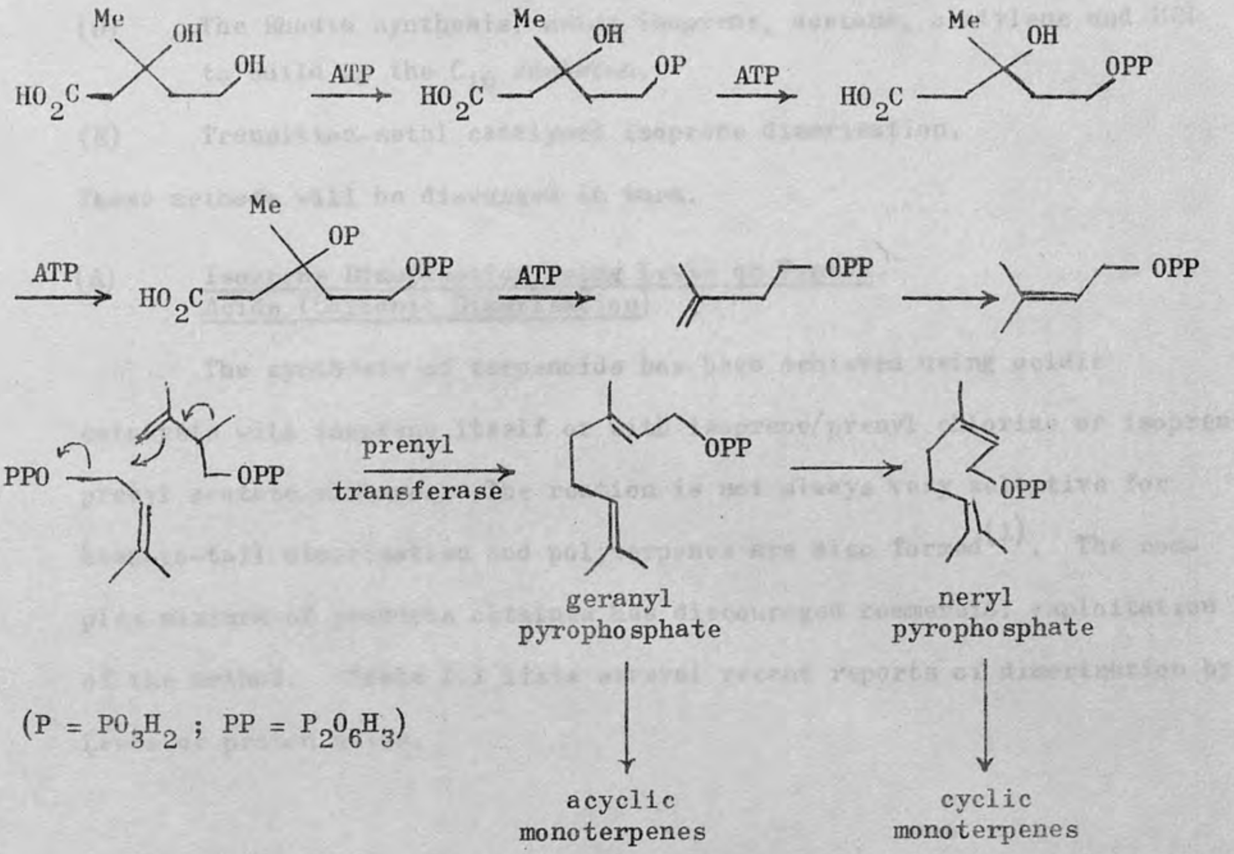
However, there are exceptions to the head-to-tail rule, particularly among the higher terpenoids, and in the 1950's Ruzicka(2,3) proposed the 'biogenetic isoprene rule'. This states that naturally occurring terpenoids are derived either directly or by way of predictable stereo-specific cyclisations, rearrangements and dimerisations from acyclic C-10, C-15, C-20 and C-30 precursors - geraniol, farnesol, geranylgeraniol and squalene respectively. This rule implies a common biosynthetic pathway for the whole family. Isoprene itself does not occur in nature, and the generally accepted route for the biosynthesis of geranyl pyrophosphate (GPP) takes (R)-(+) mevalonic acid as its starting point.



$(P = PO_3H_2 \; ; \; PP = P_2O_6H_3)$

The biosynthesis of monoterpenes has recently been reviewed$^{(4)}$.

1.1 SYNTHETIC METHODS

In principle the dimerisation of isoprene to acyclic monoterpenes would appear to be a fairly simple operation. In practice, however, several problems arise: firstly the formation of cyclic stable end-products such as dipentene and terpineols; secondly the production of trimeric and higher polymeric isoprene molecules; thirdly the production of non-head-to-tail isomers.

Several different general approaches have been used for the oligomerisation and telomerisation of isoprene. Among these are:

(A) The action of Lewis or proton acid catalysts on isoprene or isoprene/prenyl chloride mixtures (cationic dimerisation).

(B) The action of strong bases on isoprene (anionic dimerisation).

(C) Thermal dimerisation and photodimerisation of isoprene.

(D) The Rhodia synthesis, using isoprene, acetone, acetylene and HCl to build up the C_{10} skeleton.

(E) Transition-metal catalysed isoprene dimerisation.

These methods will be discussed in turn.

(A) Isoprene Dimerisation using Lewis or Proton Acids (Cationic Dimerisation)

The synthesis of terpenoids has been achieved using acidic catalysts with isoprene itself or with isoprene/prenyl chloride or isoprene/prenyl acetate mixtures. The reation is not always very selective for head-to-tail dimerisation and polyterpenes are also formed(1). The complex mixture of products obtained has discouraged commercial exploitation of the method. Table 1.1 lists several recent reports of dimerisation by Lewis or proton acids.

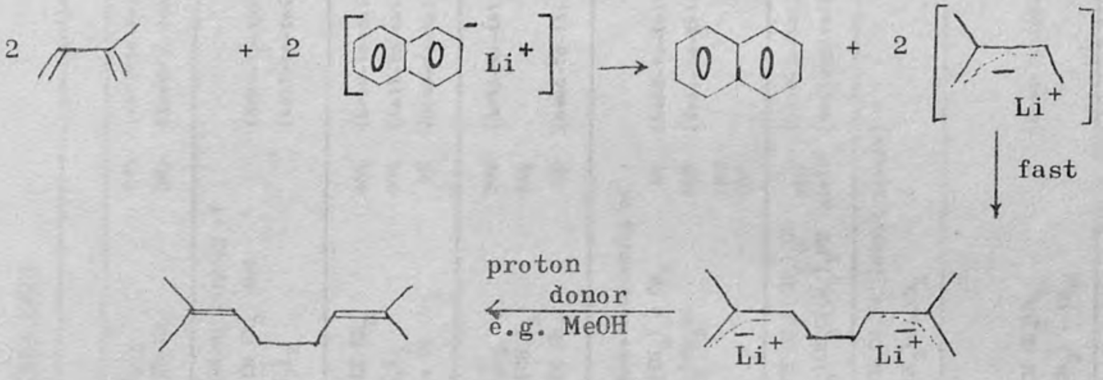
TABLE 1.1

ISOPRENE DIMERISATION WITH LEWIS OR PROTON ACIDS

CATALYST	SUBSTRATE(S)	PRODUCTS	REFERENCE
RCO_2H , $SnCl_4$	ISOPRENE and ISOPRENE/PRENYL CHLORIDE	$(H_3C)_2C = CH\ CH_2CH_2CH(OH)C(CH_3) = CH_2$ (tail-to-tail) $(H_3C)_2C = CH\ CH_2CH_2CH = C(CH_3)CH_2OH$ (tail-to-tail) also linalool, geraniol, α-terpineol	5
HCl $SnCl_4$	ISOPRENE	$(H_3C)_2C = CH\ CH_2CH_2C(CH_3) = CH\ CH_2Cl$ (50-65%) (head-to-tail) $(H_3C)_2C = CH\ CH_2CH_2C(CH_3)Cl\ CH = CH_2$ (5-10%) (head-to-tail) $(H_3C)_2C = CH\ CH_2CH(CH_2Cl)C(CH_3) = CH_2$ (7-10%) $(H_3C)_2C = CH\ CH_2CH_2CH(Cl)C(CH_3) = CH_2$ (5-7%) (tail-to-tail) α-terpinyl chloride (12-18%) $(H_3C)_2C = CH\ CH_2CH(CH_2Cl)C(CH_3)_2Cl$ (5-10%)	6
$SnCl_4$	ISOPRENE/PRENYL CHLORIDE	geraniol, linalool, α-terpineol, lavandulol	7
CONC H_2SO_4	ISOPRENE/ACETIC ACID	linalool 1% lavandulol 8% α-terpineol 29% nerol 3% geraniol 18% $H_2C = C(CH_3)CH(OH)CH_2CH_2CH = C(CH_3)_2$ 14% (tail-to-tail) $(H_3C)_2C = CH\ CH_2CH_2CH = C(CH_3)CH_2OH$ 6% (tail-to-tail)	8
H_3PO_4	ISOPRENE	$(H_3C)_2C(OH)CH = CH_2$ $(H_3C)_2C = CH\ CH_2OH$ linalool geraniol α-terpinene α-terpineol terpineol alloocimene lavandulol	9
$BF_3.Et_2O$	ISOPRENE/PRENYL ACETATE	$(H_3C)_2C = CH\ CH_2CH_2C(CH_3) = CH\ CH_2OAC$ (head-to-tail) $(H_3C)_2C = CH\ CH_2CH_2CH(OAC)C(CH_3) = CH_2$ (tail-to-tail) $(H_3C)_3\dot{C}H(CH_2OAC)CH_2CH = C(CH_3)_2$ $(H_3C)_2C(OR)CH(CH_2OAC)CH_2CH = C(CH_3)_2$ (R = H , OAC) α-terpinyl acetate	10

(B) Anionic Dimerisation and Telomerisation of Isoprene

In 1967 Suga et al(11) dimerised isoprene with lithium napthalene in THF, obtaining a 45% conversion to 2,6-dimethyl - 2,6-octadiene and 2,7-dimethyl-2,6-octadiene. Several other papers followed (see Table 1.2). The mechanism suggested(12) for this reaction involves a $C_{10}H_{14}^{2-}$ dianion:



This type of reaction is, of course, at best stoicheiometric in alkali metal.

Telomerisation of isoprene has also been achieved, using oxygen, amines or ketones as telogen (see Table 1.2). Passage of dry oxygen through a THF solution of lithium naphthalene and isoprene followed by decomposition gave 30-40% conversion of isoprene to products consisting largely of tail-to-tail alcohols(13).

The dianion intermediate shown above is similar to that postulated in the reaction of isoprene with magnesium in refluxing THF; largely tail-to-tail dimers are obtained(14):

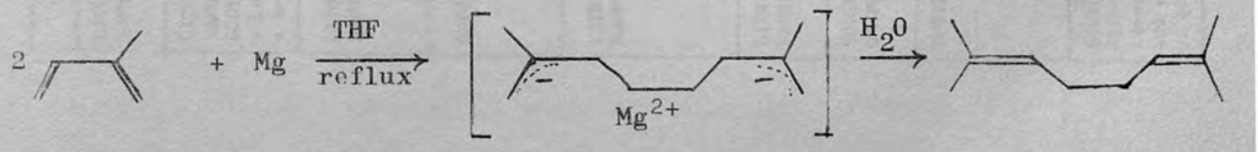


TABLE 1.2

ISOPRENE DIMERISATION WITH STRONG BASES

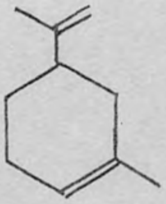
CATALYST	SUBSTRATE(S)	PRODUCTS	REFERENCE
LITHIUM NAPHTHALENE	ISOPRENE	$(H_3C)_2C = CH\ CH_2CH_2CH = C(CH_3)_2$ 50% (tail-to-tail) $(H_3C)_2C = CH\ CH_2CH_2C(CH_3) = CH\ CH_3$ 50% (head-to-tail)	11
LITHIUM NAPHTHALENE or SODIUM NAPHTHALENE + Lewis base, e.g. a t-amine	ISOPRENE	35-40% yield of dimers consisting largely of $(H_3C)_2C = CH\ CH_2CH_2C(CH_3) = CH\ CH_3$ and (head-to-tail) $(H_3C)_2C = CH\ CH_2CH_2CH = C(CH_3)_2$ (tail-to-tail)	15
LITHIUM NAPHTHALENE	ISOPRENE	$(H_3C)_2C = CH\ CH_2CH_2C(CH_3) = CH\ CH_3$ 45% (head-to-tail) $(H_3C)_2C = CH\ CH_2CH_2CH = C(CH_3)_2$ 50% (tail-to-tail) $H_2C = C(CH_3)CH_2CH_2CH_2C(CH_3) = CH\ CH_3$ 5% (head-to-tail)	16
SODIUM NAPHTHALENE	ISOPRENE	$(H_3C)_2C = CH\ CH_2CH_2CH = C(CH_3)_2$ 20% (tail-to-tail) $H_2C = C(CH_3)CH(CH_3)CH_2CH = C(CH_3)_2$ 79% $(H_3C)_2C = CH\ CH_2CH_2C(CH_3) = CH\ CH_3$ 1% (head-to-tail)	17
LITHIUM NAPHTHALENE	ISOPRENE, OXYGEN	20-30% yield of terpene alcohols consisting of $H_2C = CHC(CH_3)(OH)CH_2CH_2CH_2C(CH_3) = CH_2$ 5% (head-to-tail) $(H_3C)_2C = CH\ CH_2CH_2CH = C(CH_3)CH_2OH$ 55% (tail-to-tail) nerol 10% geraniol 10%	13
LITHIUM NAPHTHALENE	ISOPRENE AND ACETONE	$(H_3C)_2C = CH\ CH_2CH_2C(CH_3) = CH\ CH_2C(CH_3)_2OH$ 25% (head-to-tail) $(H_3C)_2C = CH\ CH_2CH_2CH = C(CH_3)CH_2C(CH_3)_2OH$ yield (tail-to-tail)	18
SODIUM, LITHIUM OR POTASSIUM	ISOPRENE and a secondary amine	$(H_3C)_2C = CH\ CH_2CH_2C(CH_3) = CH\ CH_2NR_2$ (neryl isomer) $(H_3C)_2C = CH\ CH_2CH(C(CH_3) = CH_2)CH_2NR_2$	19
BUTYL LITHIUM	ISOPRENE and a socondary amine	$(H_3C)_2C = CH\ CH_2NR_2$ $(H_3C)CH = C(CH_3)CH_2NR_2$ $(H_3C)_2C = CH\ CH_2CH_2C(CH_3) = CH\ CH_2NR_2$ (head-to-tail) $(H_3C)_2C = CH\ CH_2CH(CH_2NR_2)C(CH_3) = CH_2$	21
NICKEL NAPHTHALENE, isoprene magnesium and phosphine or phosphite	ISOPRENE	1,5-dimethyl- and 2,5-dimethyl- 1,5 cyclo octadiene (with phosphite catalyst) linear trimers, containing β-farnesene (with triphenylphosphine catalyst)	22

(C) Thermal Dimerisation and Photodimerisation of Isoprene

(i) Thermal Dimerisation

Below 100° C, thermal dimerisation at isoprene yields mainly 1-methyl-4-isopropenyl-cyclohexene (I) and 1-methyl -5-isopropenyl-cyclohexene (II). Above 200° C, increasing amounts are obtained of 1,5-dimethyl-5-vinyl-cyclohexene (III) and 1,5-dimethyl- and 2,5-dimethyl-1,5-cyclooctadiene (IV) and (V)(23).

I



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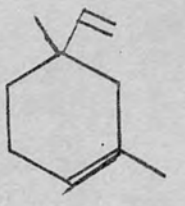

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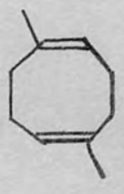

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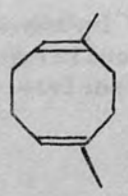
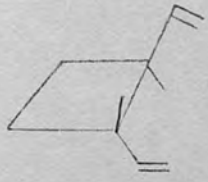


V

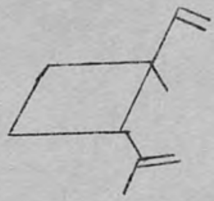
Considerable polymerisation also occurs.

(ii) Photodimerisation

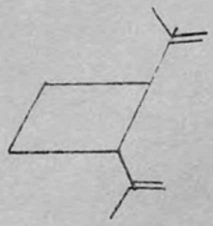
In addition to the compounds I-V, photodimerisation produces the four-membered rings (VI - VIII) (24).



VI



VII

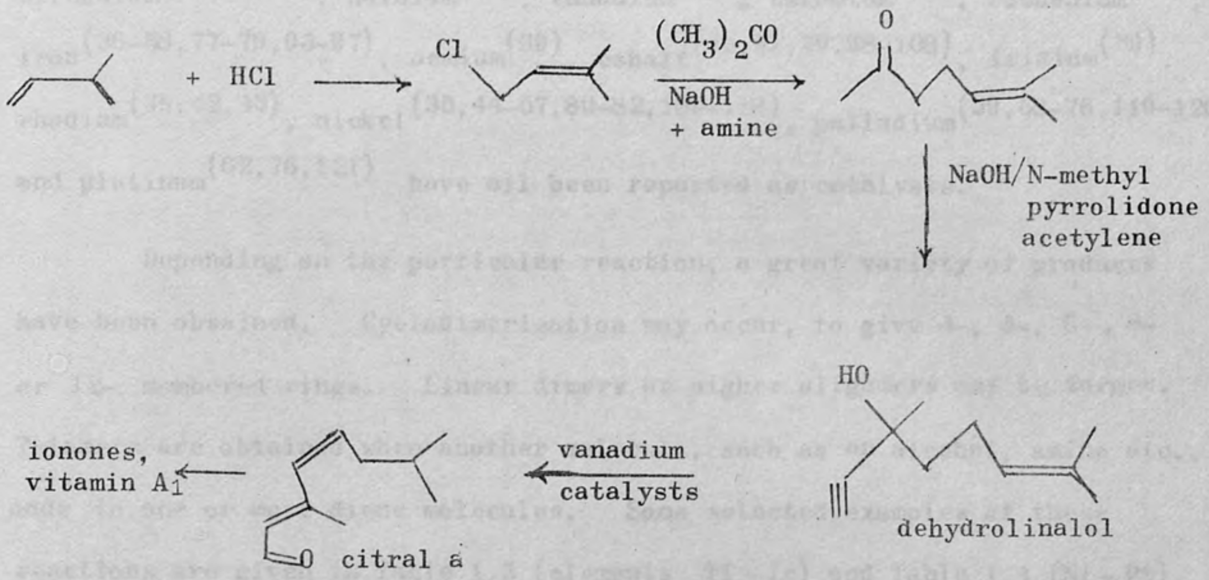


VIII

There has been no clear demonstration of the production of linear dimers by either thermal or photochemical dimerisation, although Reed reported that 1,3,7-octatriene was formed in trace amounts by heating 1,3-butadiene(25).

(D) The Rhodia Synthesis

Although addition of two molecules of isoprene is the most direct way of obtaining the C_{10} monoterpenoid skeleton, it is not the only way. In the Rhodia synthesis, for example, the skeleton is built up from isoprene, acetone and acetylene :



Ruzicka$^{(26)}$ achieved the first total synthesis of linalol using essentially this reaction sequence.

(E) Transition-Metal-Catalysed Diene Oligomerisation and Telomerisation

Oligomerisation of 1,3-dienes is catalysed by complexes of many transition metals. The Group VIII elements have been studied in most detail. Some useful reviews are available(27,28,83-86). Titanium(29-31,87-89), zirconium(32,90-92), hafnium(33), vanadium(34), chromium(35), ruthenium(39), iron(36-38,77-79,93-97), osmium(39), cobalt(40,41,79,98-108), iridium(39), rhodium(39,42,43), nickel(35,44-57,80-82,109-118), palladium(39,58-76,119-126) and platinum(62,76,121) have all been reported as catalysts.

Depending on the particular reaction, a great variety of products have been obtained. Cyclodimerisation may occur, to give 4-, 5-, 6-, 8- or 12- membered rings. Linear dimers or higher oligomers may be formed. Telomers are obtained when another molecule, such as an alcohol, amine etc., adds to one or more diene molecules. Some selected examples of these reactions are given in Table 1.3 (elements Ti - Ir) and Table 1.4 (Ni - Pt).

TABLE 1.3

TRANSITION METAL CATALYSTS IN DIENE OLIGOMERISATION

CATALYST	SUBSTRATE(S)	PRODUCTS	REFERENCE
$TiCl_4/Et_2AlCl$	Butadiene	trans, trans, cis-1,5,9 - cyclododecatriene (> 80%)	29
$TiCl_4/Et_2AlCl$	Isoprene	2,6-dimethyl-1,3,6-octatriene + cyclic products	29
$TiCl_4/Et_2AlCl$ $(PhO)_3P$	Isoprene	2,6-dimethyl - 1,3,5 - octatriene 63% 3,6-dimethyl - 1,3,6 - octatriene 2% 1,5-dimethyl-5-vinylcyclohexene 23%	30
$TiO(O^iPr)_2$ Et_2AlCl	Butadiene	1,5,9-cyclododecatriene	31
$Zr(O^tBu)_4$ Et_2AlCl PPh_3	Isoprene	2,6-dimethyl-1 - trans-3,6-octatriene	32
$Hf(O^nBu)_4$ Et_2AlCl PPh_3	Isoprene	2,6-dimethyl-1 - trans-3, 6-octatriene	33
$VO(OEt)_3$ Et_2AlCl PPh_3	Isoprene	2,6-dimethyl-1 -trans-3, 6- octatriene 3,6-dimethyl-1, 3, 6-octatriene	34
CrO_2Cl_2 $AlEt_3$	Butadiene	trans trans cis-1,5,9-cyclododecatriene 60% trans trans trans-1,5,9-cyclododecatriene 40%	35
$Fe(acac)_3$ $AlEt_3$ PPh_3	Butadiene	$H_2C = CH\ CH(CH_3)CH = CH\ CH = CH_2$ $H_2C = CH\ CH = CH\ CH_2CH = CH\ CH_3$	77
$Fe(acac)_3$ $AlEt_3$ 2,2' dipy	Butadiene	4-vinylcyclohexene 1,5-cyclooctadiene	77
$Fe(acac)_3$ $AlEt_3$	Butadiene	$H_2C = CH\ CH = CH\ CH_2CH = CH\ CH_2CH_2CH = CH\ CH_3$	78
$Fe(acac)_3$ $AlEt_3$ 2,2' dipy	Isoprene	1,5-dimethyl-1,5-cyclooctadiene 2,5-dimethyl-1,5-cyclooctadiene	79

TABLE 1.3 (continued)

TRANSITION METAL CATALYSTS IN DIENE OLIGOMERISATION

CATALYST	SUBSTRATE(S)	PRODUCTS	REFERENCE
$FeCl_3$ $AlEt_3$ PPh_3	Butadiene	3-methyl-1,4,6-heptatriene 30% 1,3,6-octatriene 70%	36
$Et_2Fe(dipy)_2$	Butadiene	1,5-cyclooctadiene 4-vinylcyclohexene	37
$Fe(acac)_3$ $AlEt_3$ 2,2' dipy	Butadiene	1,5-cyclooctadiene 4-vinylcyclohexene	38
$RhCl_3$ N_aOPh PPh_3	Butadiene and Phenol	1-phenoxy-2,7-octadiene 50%	39
$Os\ Cl_3$ NaO Ph	Butadiene and phenol	1-phenoxy-2,7-octadiene 4%	39
$CO_2(CO)_8$ $AlEt_3$	Butadiene	3-methyl-1, trans-4, 6-heptatriene	40
$CoCl_2$ $NaBH_4$ PPh_3 in EtOH	Isoprene	2,3,5-trimethyl-1,4,6-heptatriene ($PPh_3/Co < 1$) 2,7-dimethyl-1,3,7-octatriene 2,6-dimethyl-1,3,6-octatriene } ($PPh_3/Co > 1$)	41
$RhCl_3$ KOAc in ETOH	Butadiene	1,3,6-octatriene (isomerises to 2,4,6-octatriene)	42
$RhCl(PPh_3)_3$ Na O Ph	Butadiene phenol	1-phenoxy-2,7-octadiene	39
$Rh(OPh)(PPh_3)_3$	Butadiene phenol	1-phenoxy-2,7-octadiene	43
$IrH_3(PPh_3)_3$	Butadiene phenol	1-phenoxy-2,7-octadiene (< 5%)	39

TABLE 1.4

NICKEL, PALLADIUM AND PLATINUM CATALYSTS IN DIENE OLIGOMERISATION

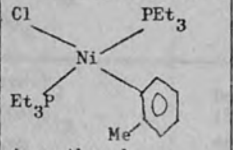
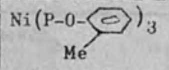
CATALYST	SUBSTRATE(S)	PRODUCTS	REFERENCE
Ni(CDT)	Butadiene	1,5,9-cyclododecatriene	44
(π-allyl)$_2$Ni	Butadiene	1,5,9-cyclododecatriene	45
[(PhO)$_3$P]$_2$Ni(AN)$_2$ in alcohol or phenol solvent	Butadiene	1,3,7-octatriene (using a phenol as solvent) 1,3,6-octatriene (using an alcohol as solvent)	46
NiEt$_2$(2,2' dipy)	Butadiene	1,5,9-cyclododecatriene	47
NiX$_2$(PPh$_3$)$_2$ (X = Cl,Br), Et Mg Br	Isoprene	2,6-dimethyl-1, trans-3, 6-octatriene (major product) 3,6-dimethyl-1,3,6-octatriene 2,7-dimethyl-1, trans-3, 6-octatriene	48
(BU$_3$P)$_2$NiCl$_2$ o-lithio-N,N-dimethylbenzylamine in methanol	Butadiene	1-vinyl-2-methylene-cyclopentane (using methanol as solvent) 4-vinyl-cyclohexene } (in absence of methanol) 1,5-cyclooctadiene } (in absence of methanol)	49
 in methanol	Butadiene	1-vinyl-2-methylenecyclopentane (50% conversion) 4-vinylcyclohexene 40% } using morpholine as solvent 1-vinyl-2-methylenecyclopentane 29% } using morpholine as solvent 1,5-cyclooctadiene 25% } using morpholine as solvent	50
	Butadiene	1,5-cyclooctadiene 4-vinylcyclohexene	80-82
Ni(AN)$_2$, PBu$_3$ in MeOH	Butadiene	$H_2C = CH\ CH = CH\ CH_2CH_2CH = CH_2$	82
Ni(AN)$_2$, P(OEt)$_3$ in MeOH	Butadiene	$H_2C = CH\ CH = CH\ CH_2CH = CH\ CH_3$	82
Ni(AN)$_2$, P(morpholide)$_3$ in MeOH	Butadiene	$(H_3C)CH = CH\ CH = CH\ CH\ CH\ CH_3$	82

TABLE 1.4 (continued)

NICKEL, PALLADIUM AND PLATINUM CATALYSTS IN DIENE OLIGOMERISATION

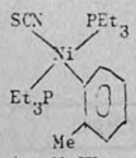
CATALYST	SUBSTRATE(S)	PRODUCTS	REFERENCE
 in MeOH	Butadiene	1,3,7-octatriene 1,5-cyclooctadiene 4-vinylcyclohexene	50
$(Bu_3P)_2NiBr_2$ $NaBH_4$	Butadiene Amine	1-vinyl-2-methylenecyclopentane butadiene-amine adducts	51
$Ni[P(OPh)_3]_4$	Butadiene Phenol	1-phenoxy-2, 7-octadiene	52
$Ni[P(OPh)_3]_4$ and $Ni[P(OEt)_3]_4$	Butadiene Phenol	1-phenoxy-2, 7-octadiene 3-phenoxy-1, 7-octadiene 1-phenoxy-trans-2-butene 3-phenoxy-1-butene	53
$Ni(acac)_2$ $PhP(O^iPr)_2$ $NaBH_4$	Butadiene ROH	1,3,7-octatriene 1-alkoxy-2,7-octatriene 3-alkoxy-2, 7 octatriene 3-alkoxy-1-butene 1-alkoxy-1-butene	54
$Ni(acac)_2$ $PhP(O^iPr)_2$ $NaBH_4$	Butadiene 1° or 2° amines, e.g. morpholine	N-2,7-octadienyl-morpholine 51% N-2-butenyl-morpholine 32% N-1 methyl-2-propenylmorpholine 15%	55
$Ni(acac)_2$	Butadiene active methylene compounds $R_1CH_2R_2$	$H_2C = CH\ CH_2CH_2CH_2CH(CHR_1R_2)CH = CH_2$ $H_2C = CH\ CH_2CH_2CH_2CH = CH\ CH_2CHR_1R_2$ $(H_3C)CH = CH\ CH_2CHR_1R_2$ $H_2C = CH\ CH(CH_3)CHR_1R_2$	56
$Ni(acac)_2$ $PhP(O^iPr)_2$ $NaBH_4$ Na O Ph	Isoprene benzyl methyl ketone	$H_2C = C(CH_3)CH(CH_3)CHPhC(O)CH_3$ 21% $(H_3C)CH = C(CH_3)CH_2CHPhC(O)CH_3$ 56% $H_2C = CH\ CH(CH_3)CH_2CH_2CH = C(CH_3)CH_2CH(Ph)C(O)CH_3$ 4% $H_2C = C(CH_3)CH_2CH_2CH_2CH = C(CH_3)CH_2CH\ Ph\ C(O)CH_3$ 19%	56
$NiBR_2$ $PhP(O^iPr)_2$	Butadiene active hydrogen compounds, RH	$H_3C\ CH = CH\ CH_2R$ $H_2C = CH\ CHR\ CH_3$ RH = morpholine $H_2C = CH\ CH_2CH_2CH_2CH = CH\ CH_2R$ di-n-propylamine $H_2C = CH\ CH_2CH_2CH_2CHR\ CH = CH_2$ benzylmethylketone	57

TABLE 1.4 (continued)

NICKEL, PALLADIUM AND PLATINUM CATALYSTS IN DIENE OLIGOMERISATION

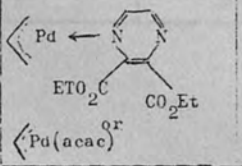
CATALYST	SUBSTRATE(S)	PRODUCTS	REFERENCE
(π-allyl)$_2$Pd$_2$Cl$_2$, NaOPh Pd(PPh$_3$)$_2$Cl$_2$, NaO Ph; etc.	Butadiene and active hydrogen compounds RH	$H_2C = CH\ CH_2CH_2CH_2CH = CH\ \ CH_2R$ ($RH = R^1OH$, ArOH, R^1CO_2H) $H_2C = CH\ CH_2CH_2CH = CH - CH = CH_2$	39 , 58
(MAA)Pd(PPh$_3$)$_2$	Butadiene and HOA$_c$ or alcohols	$H_2C = CH\ CH_2CH_2CH = CH - CH = CH_2$ $H_2C = CH\ CH_2CH_2CH_2CH = CH\ CH_2OR$ (R = Ac, Me, Et)	59
(MAA)Pd(PPh$_3$)$_2$	Butadiene and MeOD or ^{i}Pr O D	$H_2C = CH\ CHDCH_2CH_2CH = CH\ CH_2OMe$ $H_2C = CH\ CHDCH_2CH = CH - CH = CH_2$	60
(MAA)Pd(PPh$_3$)$_2$	Butadiene and R_3SiH (R = Me, Et)	$(H_3C)CH = CH\ CH_2CH_2CH = CH\ CH_2SiR_3$	61
(MAA)Pd(PPh$_3$)$_2$ Pd(PPh$_3$)$_4$ etc.	Butadiene or Isoprene and active methylene compounds $R_1CH_2R_2$	$R_1R_2CH\ CH_2CR_3 = CH\ CH_2CH_2CH_2CR_3 = CH_2$ $R_1R_2C(CH_2CR_3 = CH\ CH_2CH_2CH_2CR_3 = CH_2)_2$ (R_1 = COMe, CO_2Et; R_2 = COMe, CO_2Et; R_3 = H, Me)	62
PdBr$_2$ (Ph$_2$PCH$_2$CH$_2$PPh$_2$), NaOPh; Pd(Ph$_2$PCH$_2$CH$_2$PPh$_2$)	Butadiene and active methylene compounds $R_1CH_2R_2$	$R_1R_2CH\ CH(CH_3)CH = CH_2$ $R_1R_2CH\ CH_2CH = CH\ CH_3$ (R_1 = COMe, CO_2Et; R_2 = COMe, CO_2Et)	63
	Butadiene	1,3,6,10 dodecatetraene	64

TABLE 1.4 (continued)

NICKEL, PALLADIUM AND PLATINUM CATALYSIS IN DIENE OLIGOMERISATION

CATALYST	SUBSTRATE(S)	PRODUCTS	REFERENCE
$Pd(acac)_2$ or $Pd(OAc)_2$ $PhCH_2OK$	Butadiene acetic acid	$H_2C = CH\ CH = CH\ CH_2CG_2CH = CH_2$ $H_2C = CH\ CH_2CH_2CH_2CH = CH\ CH_2OAc$ $H_2C = CH\ CH_2CH_2CH_2CH(AOc)CH = CH_2$ $H_2C = CH\ CH_2CH = CH\ CH_2CH = CH_2$ $(H_3C)CH = CH\ CH = CH\ CH = CH\ CH_3$ using Me_2CO as solvent	65
$Pd(OAc)_2$	Butadiene	$H_2C = CH\ CH = CH\ CH_2CH = CH\ CH_2CH_2CH = CH\ CH_3$	66
$Pd(OAc)_2$ and $P\,Ph_3$	Butadiene	$H_2C = CH\ CH = CH\ CH_2CH_2CH = CH_2$	66
$Pd(ClO_4)_2$ or $Pd(BF_4)_2$	Butadiene	1,2-divinylcyclobutane	67
$Pd(ClO_4)_2$ or $Pd(BF_4)_2$ and $P\,Ph_3$	Butadiene	$H_2C = CH\ CH = CH\ CH_2CH_2CH = CH_2$	67
$PdCl_2$ $NaOAc$	Isoprene, acetic acid	$(H_3C)CH = C(CH_3)CH_2OAc$; $(H_3C)CH = C(CH_3)CH_2OAC$; $(H_3C)_2C = CH\ CH_2OA_c$ $H_2C = CH\ CH(CH_3)CH_2CH_2CH = C(CH_3)CH_2OAc$ $H_2C = CH\ CH(CH_3)CH_2CH_2C(CH_3) = CH\ CH_2OAc$ $(H_3C)_2C = CH\ CH_2CH_2C(CH_3) = CH\ CH_2OAc$	68

TABLE 1.4 (continued)

NICKEL, PALLADIUM AND PLATINUM CATALYSTS IN DIENE OLIGOMERISATION

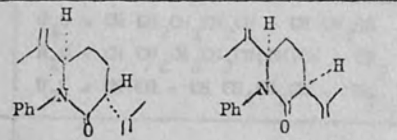
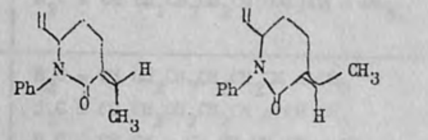
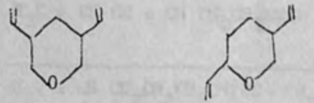
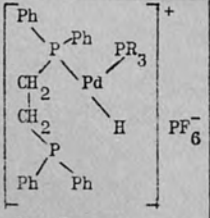
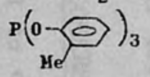
CATALYST	SUBSTRATE(S)	PRODUCTS	REFERENCE
$Pd(OAc)_2$, PPh_3	Butadiene, ammonia	$N(CH_2CH = CH\ CH_2CH_2CH_2CH = CH_2)_3$ $NH(CH_2CH = CH\ CH_2CH_2CH_2CH = CH_2)_2$	69
$PdCl_2(PPh_3)_2$ NaOPh	Butadiene, $^nPrNO_2$	$H_3C\ CH_2CH(NO_2)CH_2CH = CH\ CH_2CH_2CH_2CH = CH_2$ $H_3C\ CH_2C(NO_2)(CH_2CH = CH\ CH_2CH_2CH_2CH = CH_2)_2$	69
$(MAA)Pd(PPh_3)_2$	Isoprene PhNCO		70
$(MAA)Pd(PPh_3)_2$	Butadiene PhNCO		70
$Pd(PPh_3)_4$	Butadiene, formaldehyde		71
 R = Pr, cy	Butadiene, methanol	$H_2C = CH\ CH = CH\ CH_2CH_2CH = CH_2$ $H_2C = CH\ CH_2CH_2CH_2CH = CH\ CH_2OMe$	72

TABLE 1.4 (continued)

NICKEL, PALLADIUM AND PLATINUM CATALYSTS IN DIENE OLIGOMERISATION

CATALYST	SUBSTRATE(S)	PRODUCTS	REFERENCE
$Pd(acac)_2$, PPh_3 CO_2	Butadiene water	$H_2C = CH\ CH_2CH_2CH_2CH = CH\ CH_2OH$ $H_2C = CH\ CH_2CH_2CH_2CH(OH)CH = CH_2$ $H_2C = CH\ CH = CH\ CH_2CH_2CH = CH_2$	73
$Pd(acac)_2$ 	Butadiene acetic acid	$H_2C = CH\ CH_2CH_2CH_2CH = CH\ CH_2OAC$ $H_2C = CH\ CH_2CH_2CH_2CH(OAC)CH = CH_2$	74
$Pd(PPh_3)_2Cl_2$ Na O Pr	Butadiene formic acid	$H_2C = CH\ CH_2CH_2CH_2CH_2CH = CH_2$ $H_2C = CH\ CH_2CH_2CH_2CH = CH\ CH_3$ $H_2C = CH\ CH = CH\ CH_2CH_2CH = CH_2$	75
$Pt(PPh_3)_3$ CO_2	Butadiene	$H_2C = CH\ CH = CH\ CH_2CH_2CH = CH_2$	76
$Pt(PPh_3)_2Cl_2$ NaOPh	Butadiene, acetylacetone	$H_2C = CH\ CH_2CH_2CH_2CH(CH = CH_2)CH(COMe)_2$	62

CHAPTER II

THE MECHANISM OF DIENE OLIGOMERISATION AND TELOMERISATION BY TRANSITION-METAL CATALYSTS

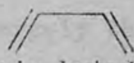
2.1 INTRODUCTION

Only in the case of nickel-catalysed cyclooligomerisations has a sufficient body of evidence begun to accrue for the general acceptance of a mechanism. This evidence is due largely to the work of Wilke et al and consists of (a) the isolation of several intermediates and (b) the detailed examination of the stereo-chemistry of the products of cyclodimerisation of methyl-substituted dienes. Confirmatory evidence has been provided by deuteration studies ; these have also shed some light on the mechanisms of oligomerisation/telomerisation reactions catalysed by palladium and other transition metals.

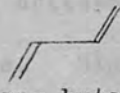
At several points in this chapter the existence of the two isomeric forms of butadiene, s-cis- and s-trans-butadiene, is invoked in the formulation of mechanisms to explain the distribution of products. Accordingly this isomerism is discussed very briefly in section 2.2 of this chapter. The nickel- and palladium-catalysed reactions are treated in sections 2.3 and 2.4 respectively, while section 2.5 surveys what is known of the mechanisms of catalysis of some other transition metals.

2.2 THE S-CIS - S-TRANS ISOMERS OF BUTADIENE AND ISOPRENE

Butadiene is recognised to exist in two planar isomeric forms:



s-cis butadiene



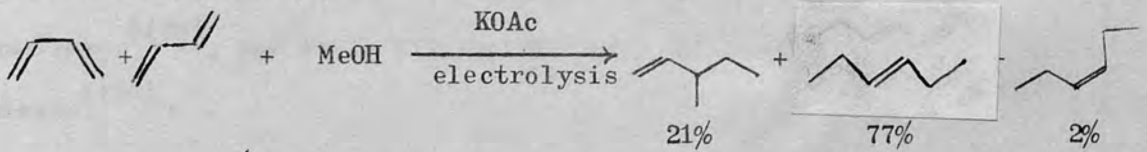
s-trans butadiene

The energy difference between the s-cis and s-trans isomers has been calculated by extended Huckel theory$^{(127)}$; the s-trans form was found to be more stable by 39.8 kJ mol^{-1}, and no activation energy was found in going from s-trans to s-cis. Earlier workers$^{(128)}$ also found the s-trans form more stable, but by only 11.6 kJ mol^{-1}. The existence of the s-cis form may be inferred from the participation of butadiene in the Diels-Alder reaction; conjugated dienes which are constrained to the s-trans form do not undergo this reaction$^{(129)}$.

Some direct evidence has been claimed for the existence of s-cis dienes:

2.2.1 Addition of Methyl Radicals to Butadiene$^{(130)}$

The existence of s-cis-butadiene was claimed to be demonstrated by the reactions (a) and (b)

(a) 

(b) 

From these product ratios, s-cis-butadiene was calculated to be present to the extent of 3-7% under the conditions used.

2.2.2 Product Variation in the Photodimerisation of Isoprene using Various Sensitisers

In the photodimerisation of isoprene using various sensitisers containing carbonyl groups it was observed that those sensitivities in which the $S_0 \rightarrow T_1$ transition occurred at or above about 293 kJ mol^{-1} produced largely four- and eight-membered ring dimers.$^{(131)}$ Sensitisers in which the transition occurred with an energy of between 222 and 293 kJ mol^{-1} produced largely the six-membered ring compounds. Since it is known that the 0-0 components of the $S_0 \rightarrow T_1$ transition of isoprene (i.e. very largely s-trans isoprene) occurs at 293 kJ mol^{-1}, it is assumed that at this energy the s-trans-isoprene radical is formed, while at lower irradiating energies the s-cis-isoprene radical is obtained (the $S_0 \rightarrow T_1$ transition in 1.3 cyclohexadiene occurs at 224 kJ mol^{-1}; the value for s-cis-isoprene is probably similar).

2.3 OLIGOMERISATION BY NICKEL CATALYSTS

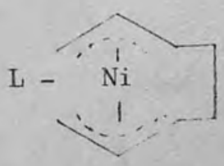
2.3.1 Cyclooligomerisation

Nickel-catalysed cyclooligomerisation of butadiene has been extensively researched(35,44,80-82,109-118,132-136,139) and reviewed(28,83,137,138). Some idea of the complexity of the system may be derived from Fig.2.1. Compound I is obtained by triethyl aluminium reduction of nickel acetylacetonate in the presence of butadiene. If excess butadiene is used the reaction proceeds catalytically, yielding all-trans-CDT (major product), cis-trans-trans-CDT and cis-cis-trans-CDT(133). Although the all-cis-isomer is not obtained in this reaction, it may be prepared from the all-trans-isomer(139), and in fact forms the most stable of the (CDT)Ni complexes(134):

$$\text{(all-trans-CDT)Ni} + \text{(all-cis-CDT)} \rightarrow \text{(all-cis CDT)Ni} + \text{all-trans-CDT}.$$

The C_{12} chain in I may also be closed by stoicheiometric addition of triethylphosphine and the complex II is isolable(44). The factors governing the ratios of all-trans-, cis-trans-trans- and cis-cis-trans-isomers have been discussed(83). One suggestion is that the ratio of s-cis- to s-trans- butadiene is important.

By blocking one of the coordination sites around the nickel atom with, for example, a phosphine, cyclodimers may be obtained instead of cyclotrimers(35) (in fact, Reed(132) in 1954 obtained 30-40% yield of 1,5-COD using Reppe-type catalysts). Thus, reduction of nickel acetylacetonate at low temperatures in the presence of a phosphine or phosphite and butadiene yields the complex III which is an active catalyst for the formation of cis,cis-1,5-cyclooctadiene (yields over 95%).



III

For $L = P(O(O-C_6H_4-C_6H_5))_3$, complex III has been isolated and characterised(35); treatment of III at low temperatures with diethyl aluminium hydride and subsequent warming to 20° gives 80% of the expected amount of n-octane, strongly suggesting that the C_8 chain in III is unclosed.

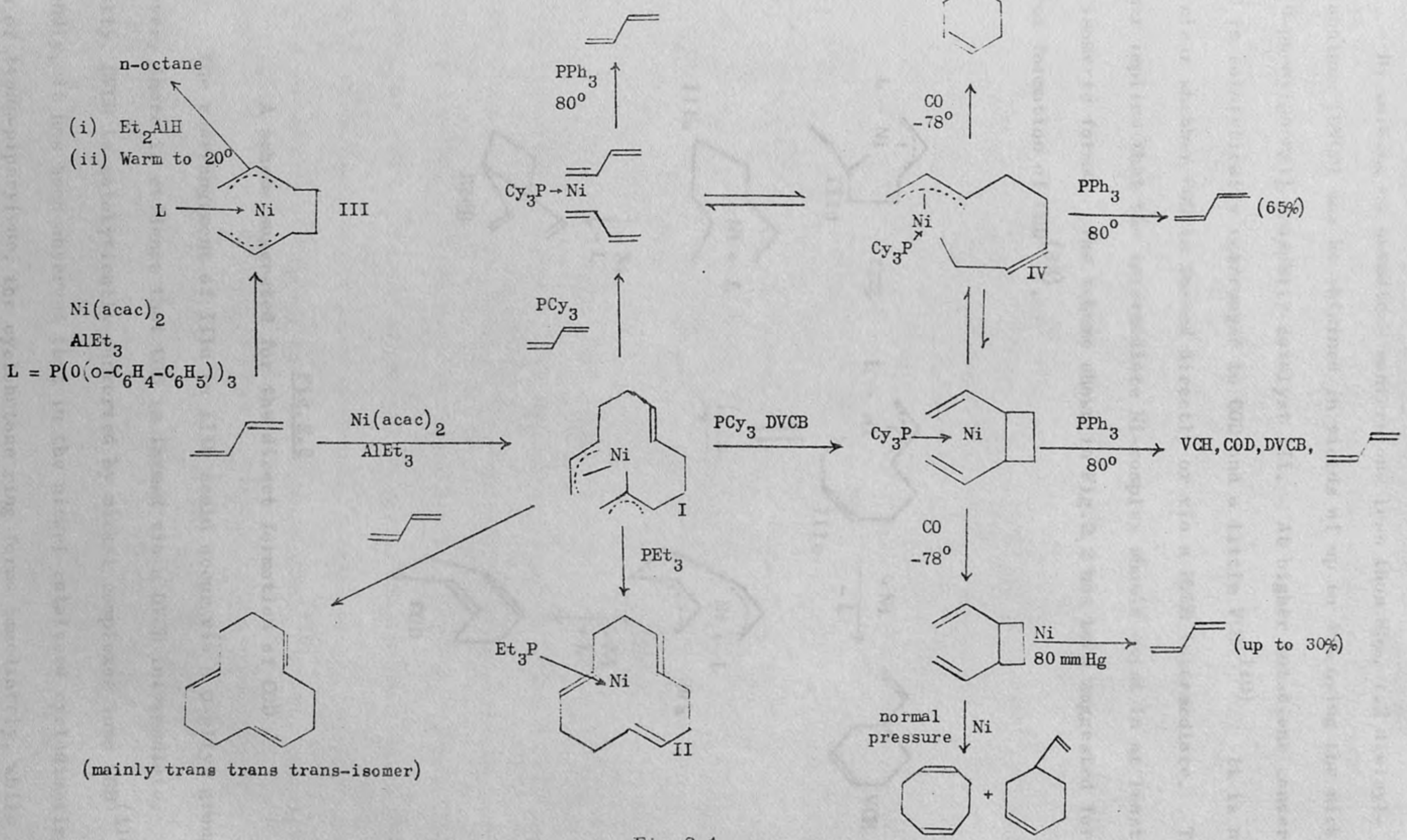


Fig. 2.1
Some nickel-catalysed reactions of butadiene

By working at butadiene conversions less than 85%, 1.2 divinylcyclobutane (DVCB) may be obtained in yields of up to 40% using the nickel tri(O-phenylphenyl) phosphite catalyst III. At higher butadiene conversions DVCB is catalytically rearranged to COD and a little VCH$^{(110)}$. It is not yet clear whether COD is formed directly or via a DVCB intermediate. The former implies that the intermediate Ni-complex should exist in at least two isomeric forms. The scheme shown in Fig.2.2 has been suggested for direct formation of COD$^{(83)}$.

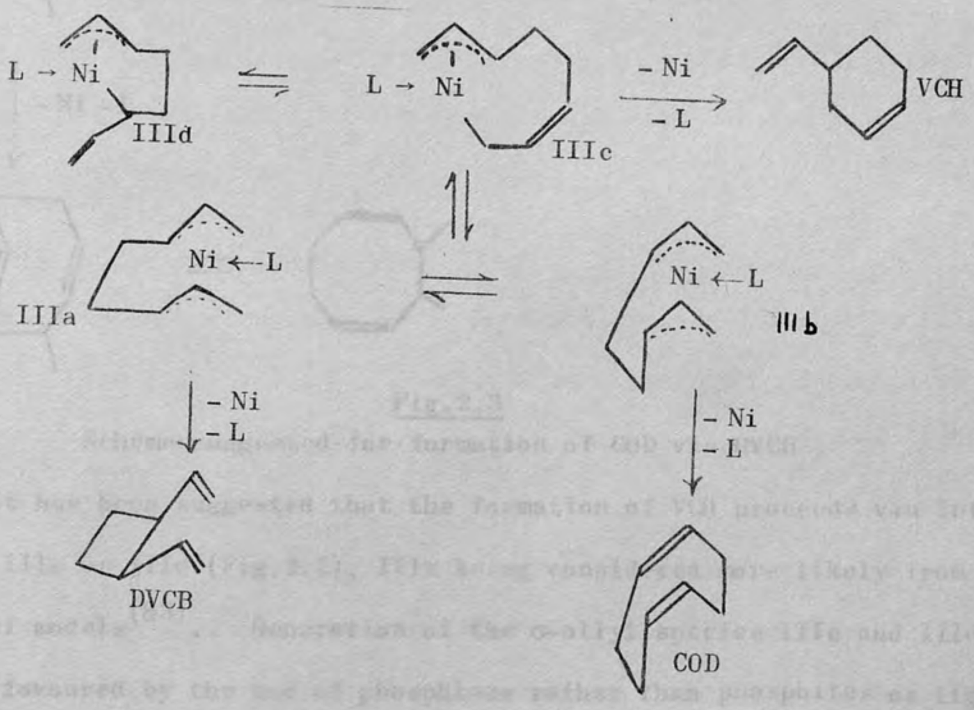


Fig.2.2

A scheme suggested for the direct formation of COD

The rearrangement of IIIa to IIIb could occur via a σ-allyl group. However, there is evidence that COD is formed via a DVCB intermediate. Firstly, DVCB is catalytically converted by nickel complexes into COD$^{(110)}$. Secondly, it has been observed that in the nickel-catalysed cyclodimerisation of trans-piperylene, the cyclobutane ring forms immediately, while formation of the dimethyl-cyclooctadiene requires an induction period of approximately one hour. Fig.2.3 depicts the mechanism postulated for the reaction.

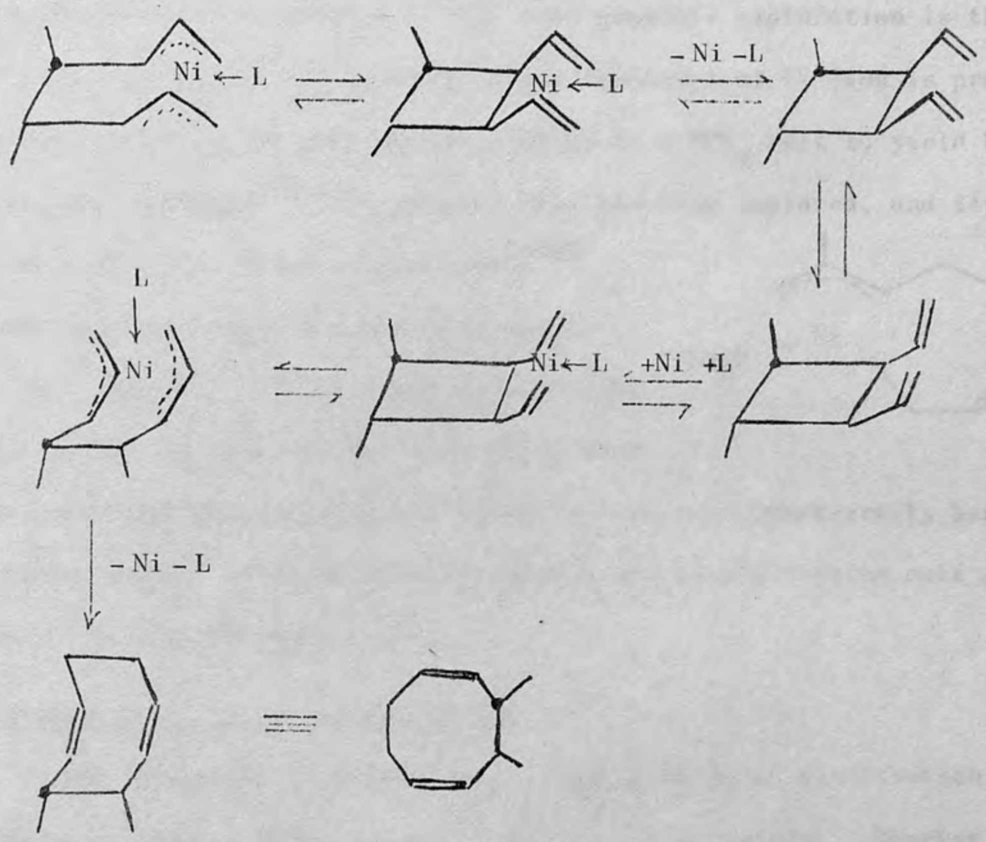
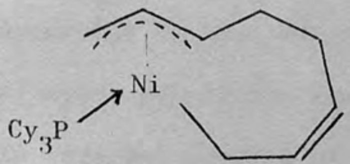
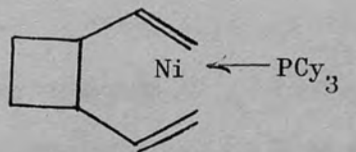


Fig.2.3
Scheme suggested for formation of COD via DVCB

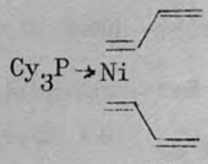
It has been suggested that the formation of VCH proceeds via intermediates IIIc or IIId (Fig.2.2), IIIc being considered more likely from studies of models(83). Generation of the σ-allyl species IIIc and IIId would be favoured by the use of phosphines rather than phosphites as ligands, since the former are better electron donors. The increase in yields of VCH by using phosphines as ligands has been demonstrated(110). The existence of the complex IV in solution has been indicated by spectroscopic studies(111,136); it is formed by the rearrangement in solution of complexes



IV

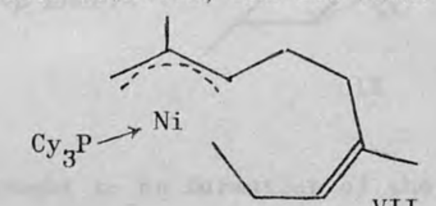


V



VI

V or VI. Indeed, the structure of VI in the solid state has been contested by Brown et al(111), who regard it as having the structure IV (i.e. the solution-state structure). The most probable explanation is that VI is a low-temperature intermediate in the formation of IV (and is probably also implicated in the decomposition of IV in a PPh_3 melt to yield butadiene). The isoprene analogue of IV, complex VII, has been isolated, and its structure determined by X-ray diffraction(140). The nmr spectrum suggested the same structure in solution. The 2, 6 positions of the methyl groups is interesting, suggesting that before coupling the two isoprene molecules are not symmetrically bonded to the nickel atom. Treatment of VII with a triphenylphosphine melt gave isoprene in over 90% yield.



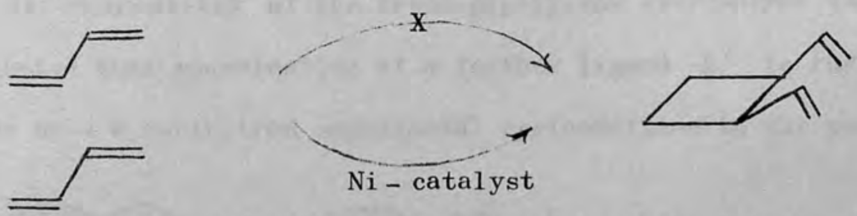
VII

The Mechanism of Cyclooligomerisation

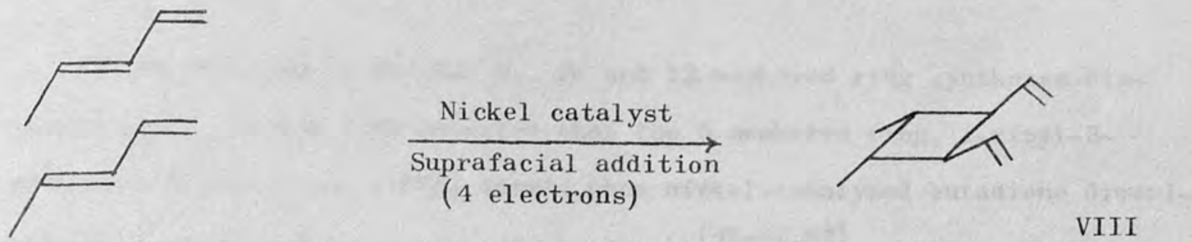
The reactions discussed above suggest that the dimerisation of butadiene on nickel catalysts has a multi-step mechanism. However, an alternative concerted mechanism has been advanced as a possibility(141-144).

Concerted Mechanism

The suprafacial cycloaddition of two butadiene molecules to give divinylcyclobutane is a symmetry-forbidden process in the ground state(145). It is suggested that interaction of the butadiene electronic orbitals with those of a nickel atom can render the cycloaddition symmetry allowed.

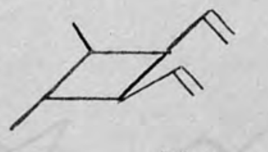


According to this theory, the nickel-catalysed head-to-head cyclodimerisation of trans-piperylene would be expected to yield the four-membered ring VIII. In fact the product of this reaction has been shown(138,140) to be IX. In the light of this and other evidence from the cyclodimerisation of methyl-



VIII

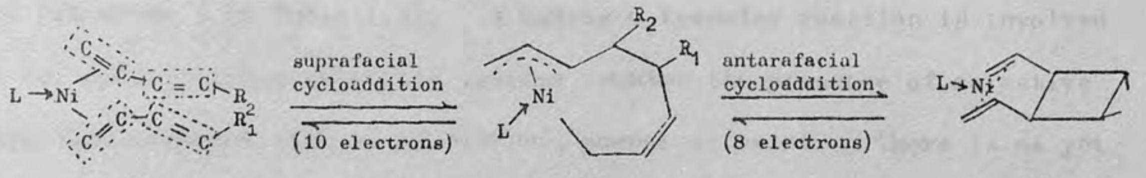
substituted dienes(140), a multistep mechanism is favoured in which two molecules complex to the metal atom and react together to form a π-allyl C_8 chain which in a final step undergoes ring closure.



IX

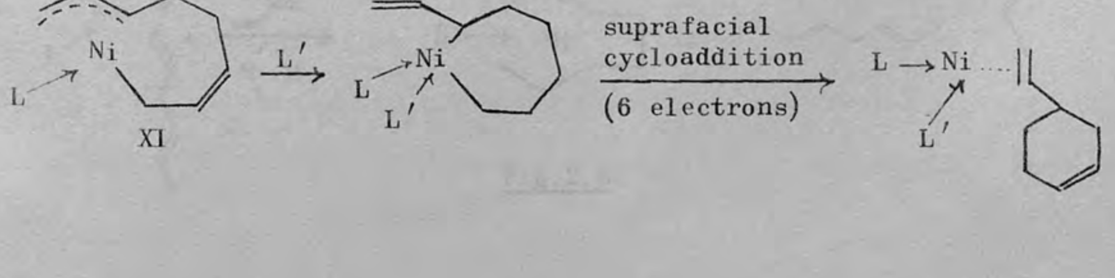
Multistep Process

In this mechanism the first step is thought to be formation of the trigonal nickel complex X from one molecule each of s-cis and s-trans butadiene (see Fig.2.4). The complex X is transformed into XI by a symmetry-allowed suprafacial cycloaddition involving 10 π-electrons (4 from each diene molecule and 2 from the metal), accompanied by oxidation at the nickel atom. An 8 π-electron antarafacial cycloaddition follows, in which the nickel atom is reduced to Ni(0) again, and a cyclobutane ring (with the stereochemistry shown) is formed. This reaction mechanism explains the stereochemistry of the trans-piperylene cyclo-dimer IX. It is also suggested that coordination of a further ligand L′ to the complex XI leads by a 6 π-electron suprafacial cycloaddition to the product VCH.

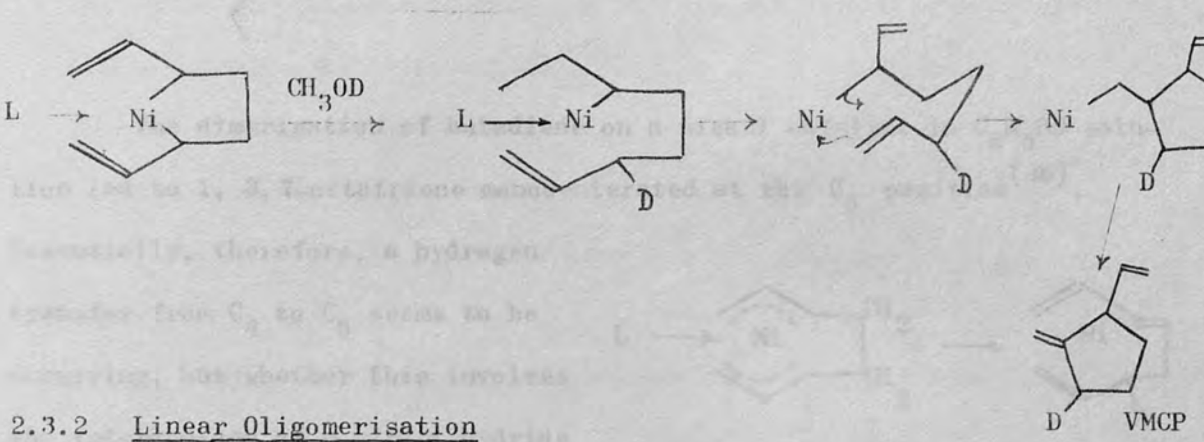


X XI XII

Fig. 2.4



In addition to the 4-, 6-. 8- and 12-membered ring syntheses discussed above, it has been reported that the 5-membered ring, 1-vinyl-3-methylene-cyclopentane (VMCP) formed when nickel-catalysed butadiene dimerisation is performed in an alcohol as solvent(49-51,82). Using MeOD as solvent, the product was found to be monodeuterated in the C_3 position. The mechanism suggested(49) is :



2.3.2 Linear Oligomerisation

Many examples are known of nickel-catalysed linear oligomerisation of butadiene (see Table 1.4). A hydrogen-transfer reaction is involved here, and all these catalytic systems require the presence of an active hydrogen compound such as an alcohol, phenol or amine. There is as yet no experimental evidence for a nickel-hydride intermediate, although this would seem a distinct possibility.

A mechanism advanced(83) for the reaction of butadiene with a nickel catalyst in the presence of a secondary amine is shown in Fig.2.5.

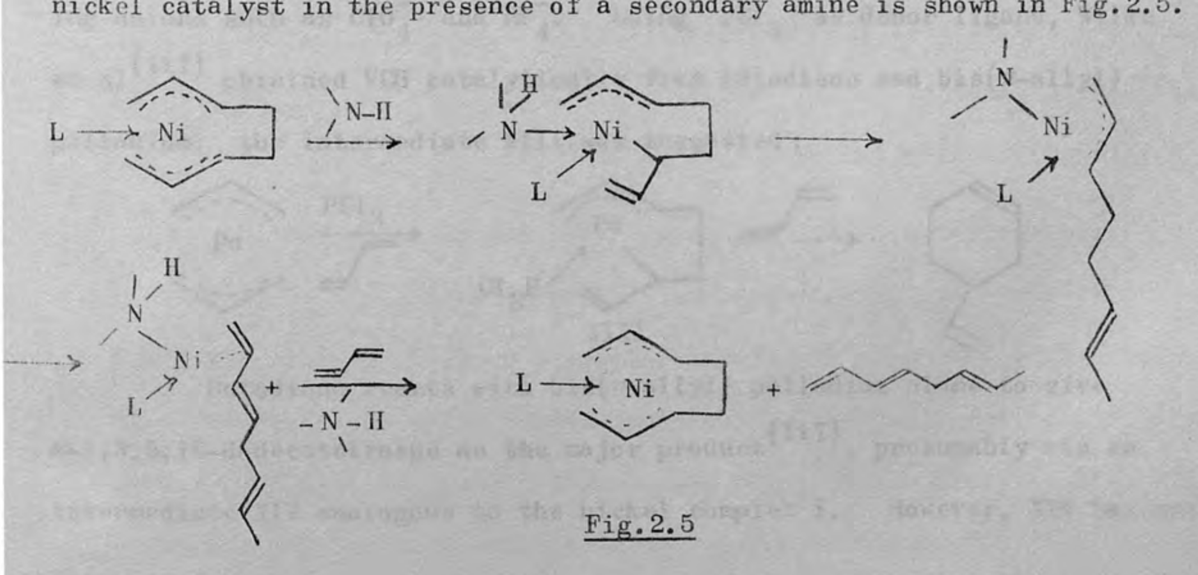
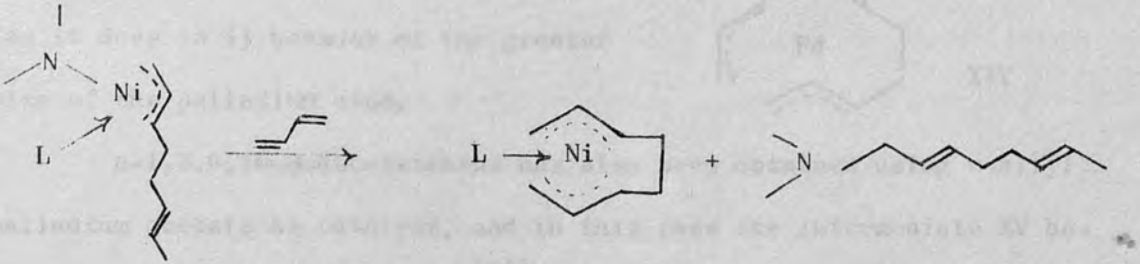
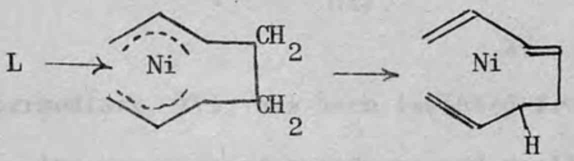


Fig.2.5

This mechanism receives some support from the formation in a side reaction of a trialkylated amine :



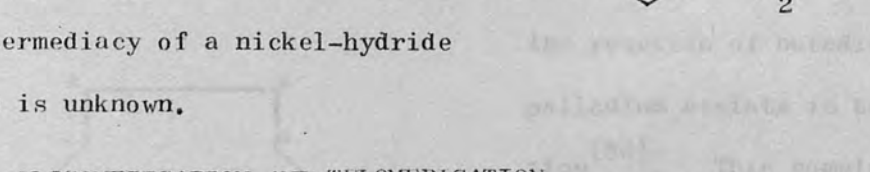
The dimerisation of butadiene on a nickel catalyst in C_6H_5OD solution led to 1, 3, 7-octatriene monodeuterated at the C_6 position(46). Essentially, therefore, a hydrogen transfer from C_4 to C_6 seems to be occurring, but whether this involves the intermediacy of a nickel-hydride species is unknown.



2.4 OLIGOMERISATION AND TELOMERISATION BY PALLADIUM CATALYSTS

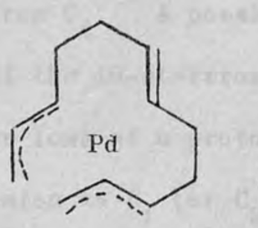
2.4.1 Oligomerisation

Only a few cases of palladium-catalysed cyclooligomerisation have been reported. A mixture of divinylcyclobutanes was found(67) to result from the reaction of butadiene with salts of palladium with weakly complexing anions such as ClO_4^- and BF_4^-. Using PCl_3 as donor ligand, Wilke et al(117) obtained VCH catalytically from butadiene and bis(π-allyl) palladium; the intermediate XIII was suggested :



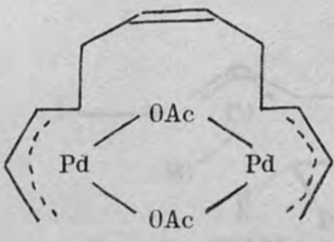
XIII

Butadiene reacts with bis(π-allyl) palladium alone to give n-1,3,5,10-dodecatetraene as the major product(117), presumably via an intermediate XIV analogous to the nickel complex I. However, XIV has not been isolated. It may be supposed that the C_{12} chain in XIV does not link ends (as it does in I) because of the greater size of the palladium atom.



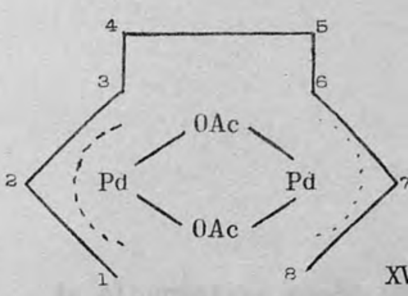
XIV

n-1,3,6,10-Dodecatetraene has also been obtained using π-allyl palladium acetate as catalyst, and in this case the intermediate XV has been isolated and characterised(66). Thus there seems to be two separate trimerisation mechanisms available since both XIV and XV yield the same product.

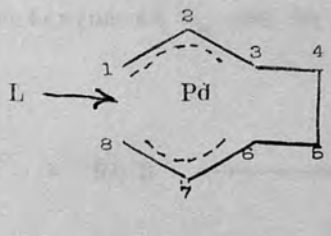


XV

Another acetato-bridged intermediate, XVI, has been isolated from the reaction of butadiene and π-allyl palladium acetate in acetic acid solution(66). This complex is an intermediate for the dimerisation of butadiene to octatriene. By analogy with nickel one would expect to find the C_8 π-allyl complex XVII, but this has not as yet been isolated, although experimental results have been explained using mechanisms involving XVII or its π, σ-bonded analogue XIII.



XVI



XVII

Linear dimerisation involves a hydrogen transfer, generally accepted to be from C_4 to C_6 in XVI or XVII, and yielding 1,3,7-octatriene. when butadiene was dimerised on a palladium catalyst using $(CH_3)_2CHOD$ as solvent, the product triene was monodeuterated at C_6, and the reaction proceëded much faster than when an aprotic solvent was used(119). Thus the rate of triene formation appears to be enhanced, presumably by addition of a proton from the alcohol to C_6, followed by loss of a proton from C_4. A possible mechanism is shown in Fig.2.6. After formation of the 16-electron complex XVIII, two possibilities are available, either loss of a proton from C_4 to give octatriene, or addition of the alkoxy anion to C_1 (or C_3) to give the alkoxy-octadiene. The ratios of these products could be expected to vary with R, as is found in practice.

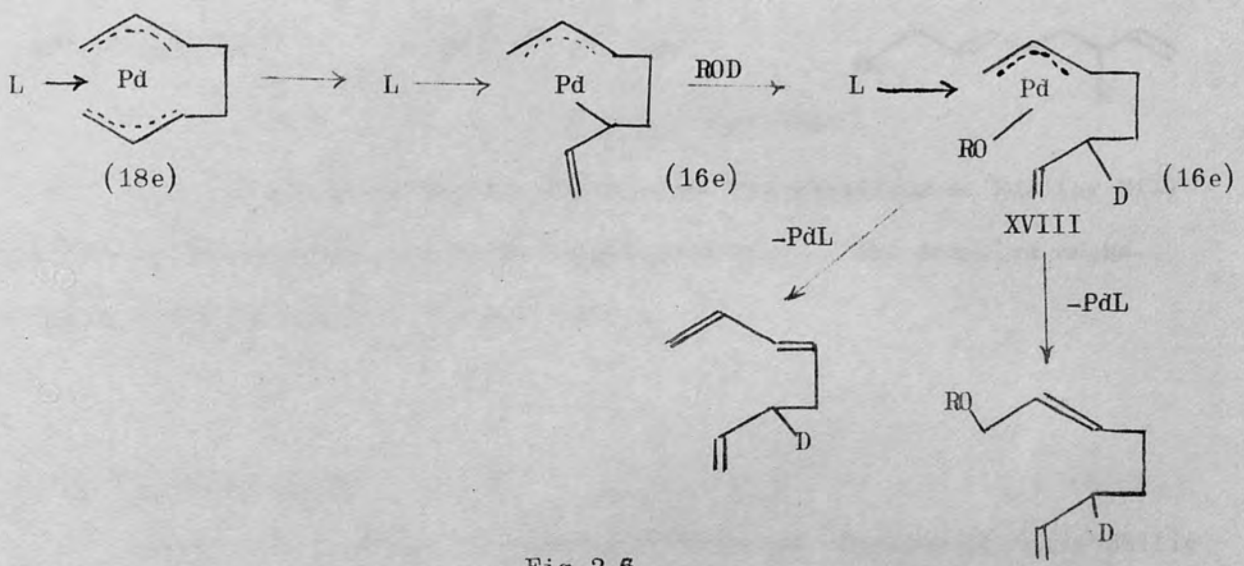


Fig.2.6

An alternative route to the triene/alkoxydiene products has been suggested(86). This involves a hydride intermediate, and the incorporation of deuterium at C_6 can be explained (Fig.2.7).

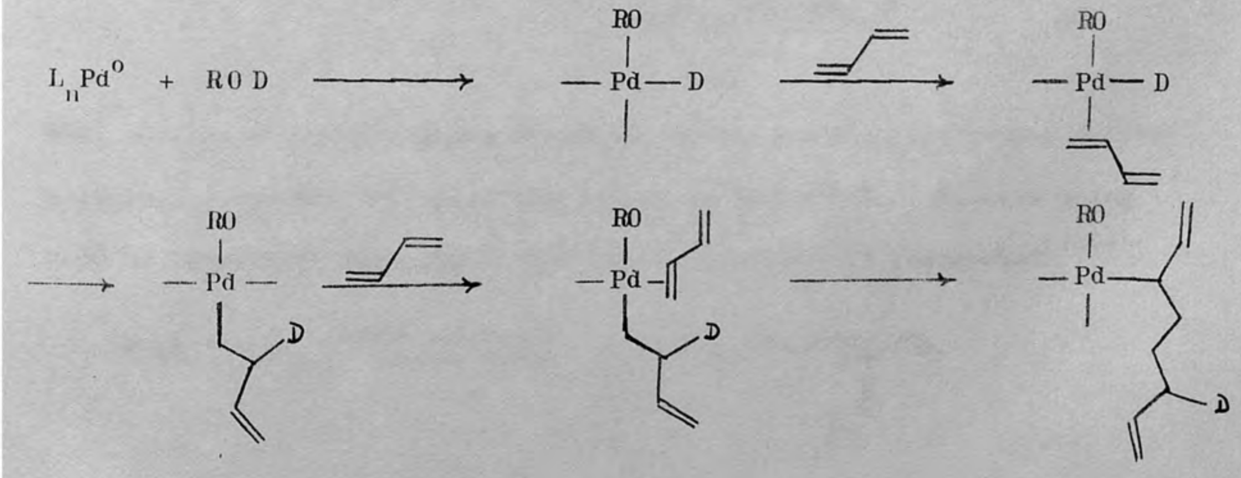


Fig.2.7

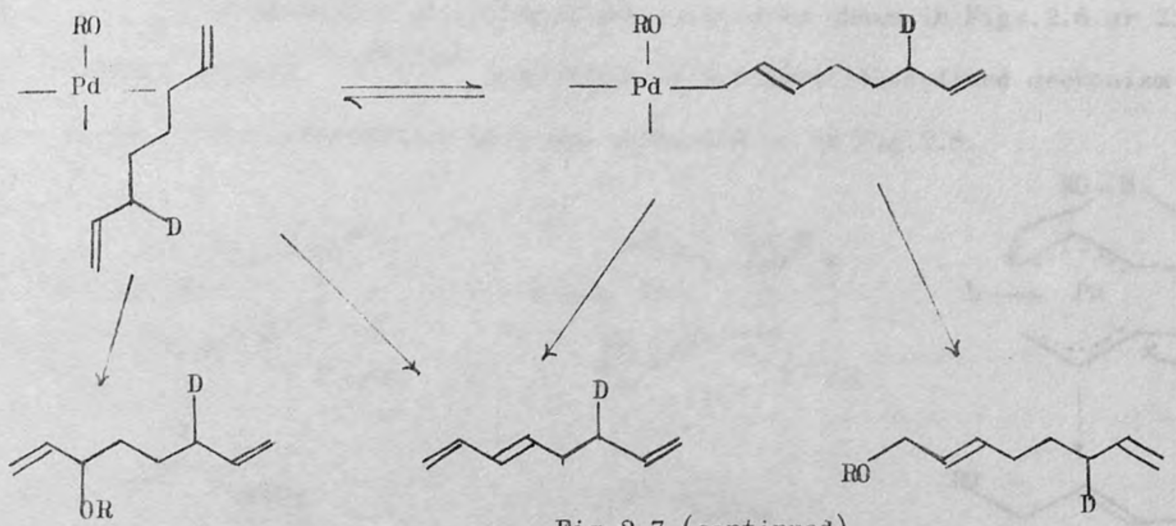
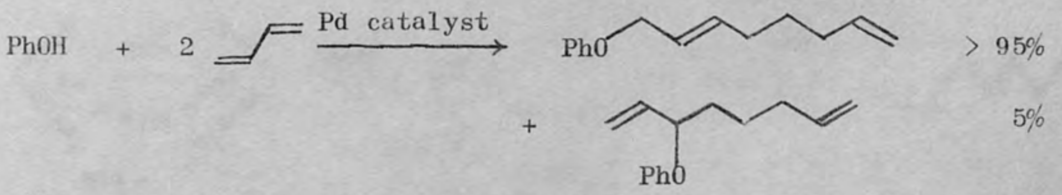


Fig. 2.7 (continued)

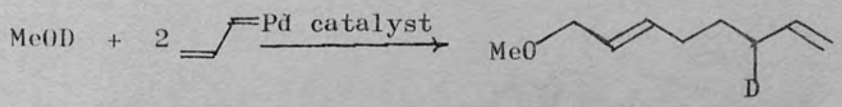
As yet there is no direct evidence for the existence of Pd- (or Ni-) hydrides as intermediates in diene oligomerisations. The detailed mechanisms must remain a matter for speculation.

2.4.2 Telomerisation

Linear dimerisation accompanied by terminal addition of nucleophilic groups were first reported by Smutny et al(39,58). For example, palladium catalysts were very efficient in the formation of 1-phenoxyoctadiene from phenol and butadiene :



Many similar reactions, using alcohols, amines, carboxylic acids, active methylene compounds and water are listed in Table 1.4. Studies using MeOD as cotelomer have shown that the C_6 position is deuterated(120) :



The formation of telomers may proceed as shown in Figs.2.6 or 2.7. Several authors$^{(46,60,119)}$ have advanced a rather ill-defined mechanism based on the intermediate XVII and portrayed as in Fig.2.8.

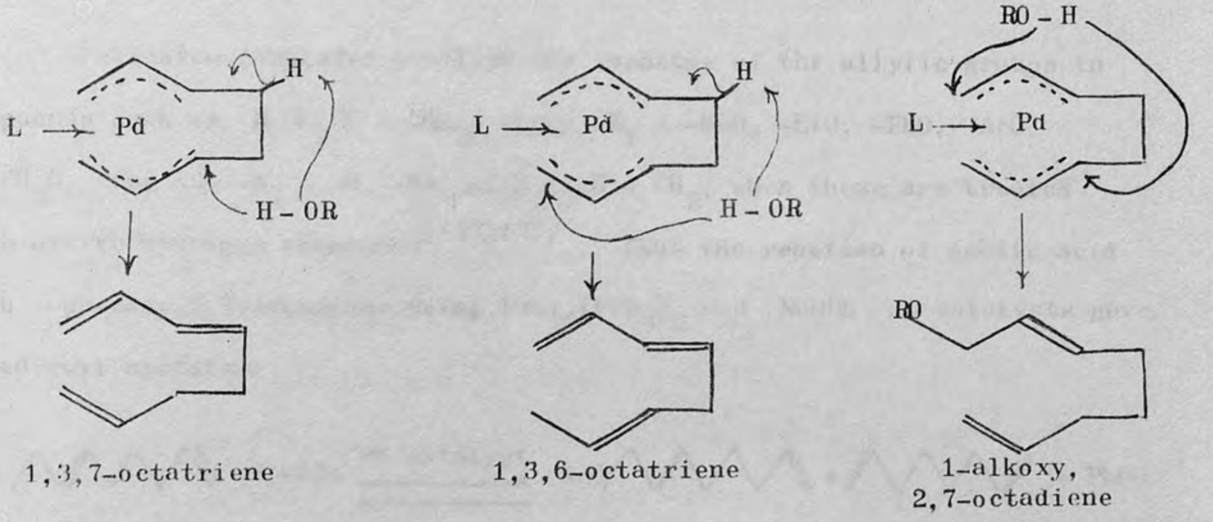


Fig.2.8

An alternative mechanism based on a complex of the type XVIa has been suggested$^{(39)}$ for the telomerisation of butadiene with phenol to give phenoxyoctadiene and octatriene (Fig.2.9). This figure also shows the equilibrium existing between the octatriene and the phenoxyoctadiene; the

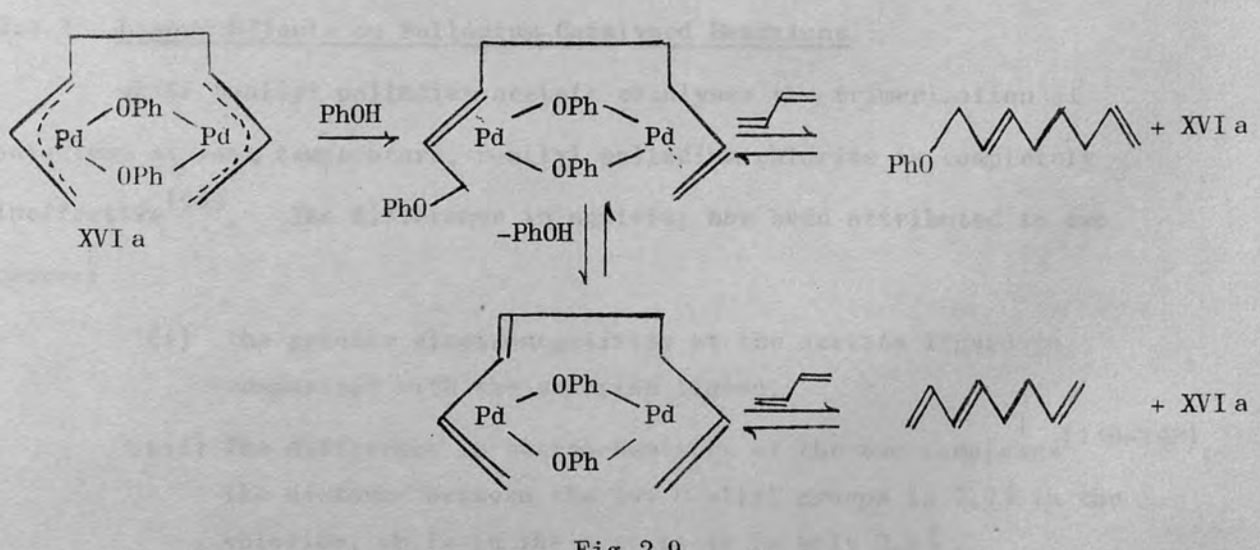
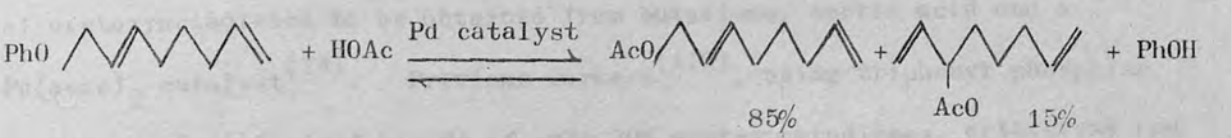


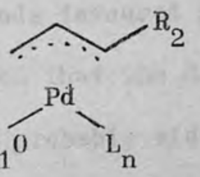
Fig.2.9

latter may easily be decomposed to phenol and the octatriene with a palladium catalyst under suitable conditions such as reduced pressure, where the products are removed as they are formed$^{(39)}$.

Palladium complexes catalyse the exchange of the allylic groups in compounds such as $R_1CH_2CH = CHR_2$, where $-R_1 = -MeO, -EtO, -PhO, -AcO, -PhCH_2O$, etc. and $-R_2 = -H, -Me, -(CH_2)_3CH = CH_2$, when these are treated with active hydrogen compounds$^{(122,123)}$. Thus the reaction of acetic acid with 1-phenoxy-2,7-octadiene using $PdCl_2(PPh_3)_2$ and NaOPh as catalysts gave octadienyl acetates:



The reaction was reversible, and was suggested to proceed via oxidative addition of the allylic carbon-oxygen bond to the palladium atom, giving a complex of type XX.



$(-R_2 = -(CH_2)_3CH = CH_2)$

2.4.3 Ligand Effects on Palladium-Catalysed Reactions

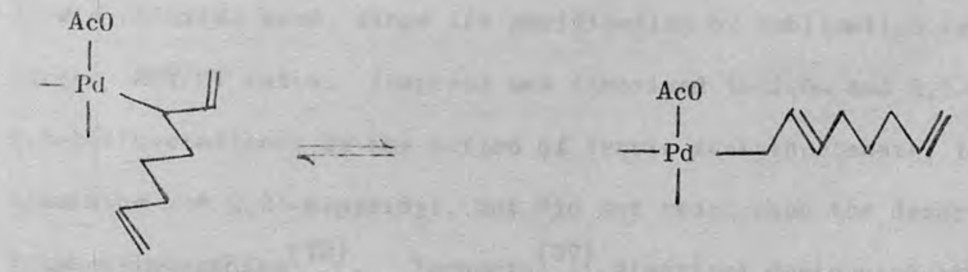
While π-allyl palladium acetate catalyses the trimerisation of butadiene at room temperature, π-allyl palladium chloride is completely ineffective$^{(66)}$. The difference in activity has been attributed to two causes:

(i) The greater electronegativity at the acetato ligand in comparison with the chloride ligand.

(ii) The difference in stereochemistry of the two complexes$^{(146-148)}$; the distance between the two π-allyl groups is 7.7 Å in the chloride, while in the acetate it is only 2.9 Å.

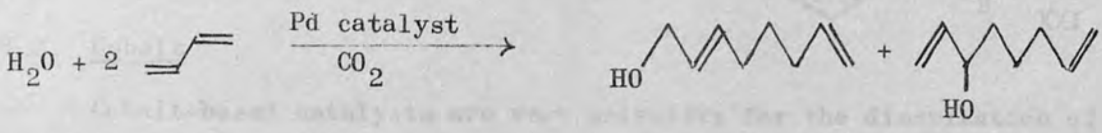
It has been observed by many workers that palladium complexes containing chloride as ligand are not active as diene oligomerisation catalysts unless an equimolar or larger amount of a base is present; sodium phenoxide, sodium acetate and potassium hydroxide have been used. The function of the base is not clear, but it probably acts by removing the chloride ion from the coordination sphere of the palladium.

Several papers have described the effect of phosphine or phosphite ligands on the yields and ratio of products. It seems desirable to add a donor ligand of some type to retain homogeneous conditions; in its absence palladium metal separates easily. The use of o-alkyl- or o-aryl-substituted triaryl phosphites as ligands enabled almost quantitative yields of acetoxyoctadienes to be obtained from butadiene, acetic acid and a $Pd(acac)_2$ catalyst(74). Previous workers(119), using triphenyl phosphine as ligand, had obtained yields of only 30% acetoxyoctadienes, octatriene and butenylacetates being also obtained. Varying the ligand also has an effect on the ratio of 1-acetoxy- to 3-acetoxy-octadiene; the o-substituted triarylphosphite ligands favoured production of the 1-acetoxyoctadiene(74). The same workers showed that the 3-substituted isomer is obtained from the 1-substituted isomer, probably via the equilibrium:



and that this equilibrium is attained much more slowly with the bulky o-substituted triaryl phosphites than with triphenyl phosphine. The use of a tertiary amine as solvent increases the yield of acetoxyoctadienes very markedly(125).

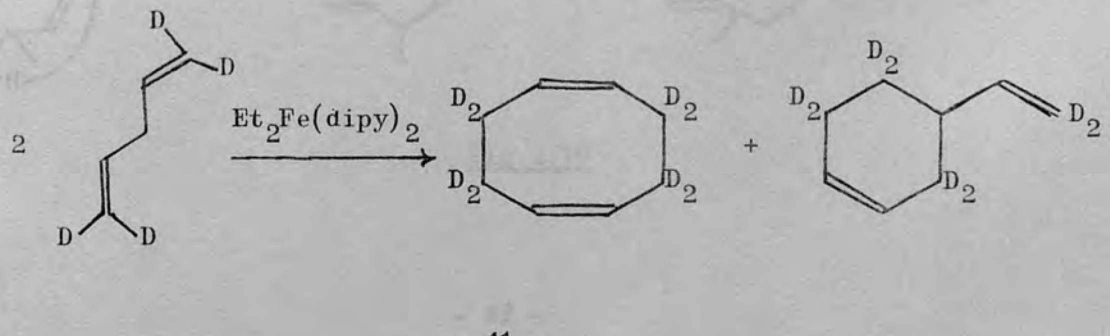
A puzzling effect of carbon dioxide has been reported in two cases. Addition of CO_2 to a $Pt(PPh_3)_3$ or $Pd(PPh_3)_4$ catalyst dimerised butadiene to 1,3,7-octatriene, while the complexes alone were inactive(76). The telomerisation of water with butadiene has been achieved(73) using palladium catalysts in the presence of CO_2; in its absence 1,3,7-octatriene was by far the major product. The fact that very low levels of CO_2 enhance the reaction rate suggests that its effect may be directly on the catalyst.



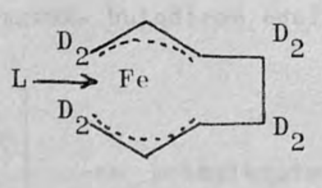
2.5 THE MECHANISM OF DIENE OLIGOMERISATION BY SOME OTHER TRANSITION METALS

2.5.1 Iron

Ferric acetylacetonate and triethyl aluminium have been found(78) to oligomerise butadiene in benzene solution to n-1,3,6,10-dodecatetraene, 1,5-cyclooctadiene, 3-methyl-1,4,6-heptatriene and n-1,3,6-octatriene. A paramagnetic iron (0) species was considered to be the intermediate. When ferric chloride was reduced by triethylaluminium in the presence of triphenylphosphine and butadiene, linear dimers were obtained(36). The major products were 1,3,6-octatriene and 3-methyl-1,4,6-heptatriene. The ratio of these dimers appeared to be affected by traces of water in the ferric chloride used, since its purification by sublimation resulted in a larger MHT/OT ratio. Isoprene was dimerised to 1,5- and 2,5-dimethyl-1,5-cyclooctadienes by the action of ferric acetylacetonate, triethyl aluminium and 2,2'-dipyridyl, but did not react when the donor ligand was triphenylphosphine(79). Yamamoto(37) dimerised deuterated butadiene $D_2C = CH - CH = CD_2$ on an iron catalyst to give exclusively the products shown



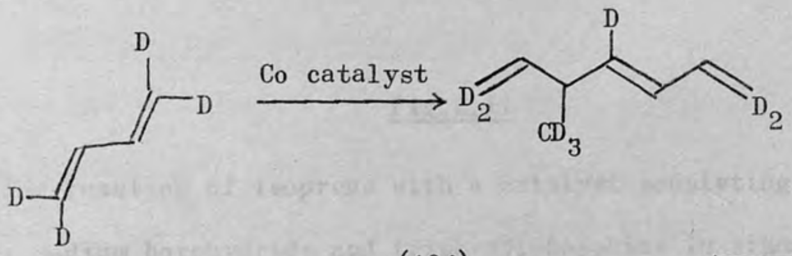
These would arise through a 'Wilke-type' intermediate XXI; there appears to be no other evidence for a mechanism.



XXI

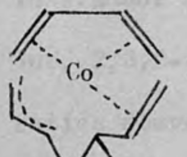
2.5.2 Cobalt

Cobalt-based catalysts are very selective for the dimerisation of butadiene to 3-methyl-1,4,6-heptatriene. $Co(acac)_3$ (101,105,108) $Co_2(CO)_8$ (40,100,102), tris (π-allyl)-cobalt(102) and 2,2'-dipyridyldiethylcobalt(103,107) have all been used as catalysts, with triethyl aluminium as the reducing agent. In all cases MHT was the major product, but n-octatrienes were also obtained. Dimerisation of $D_2C = CH - CH = CD_2$ with cobalt catalysts yielded the product XXII.



XXII

A complex XXIII has been isolated(104) from the reaction at -30° C of cobalt chloride, butadiene and sodium borohydride in ethanol; this complex also dimerises butadiene to MHT.



XXIII

Its X-ray analysis(149) confirmed the structure shown. A medium for the formation of MHT, involving a hydrogen shift, possibly through a cobalt-hydride intermediate, has been suggested(149) (Fig.2.10).

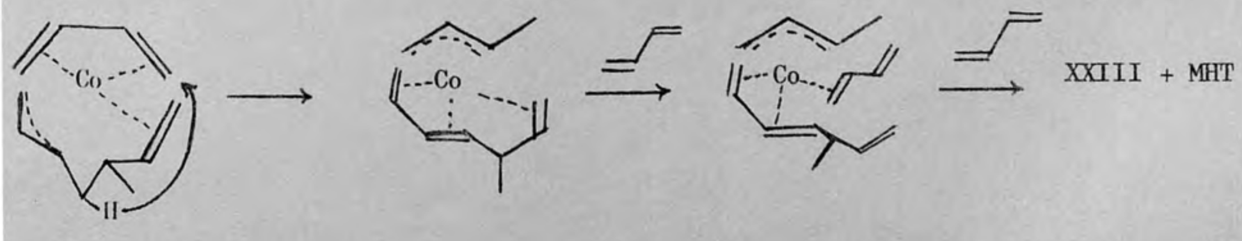


Fig.2.10

It has been suggested(150) that the ratio of octatriene to methylheptatriene formed is governed by the s-cis- s-trans- butadiene equilibrium (Fig.2.11).

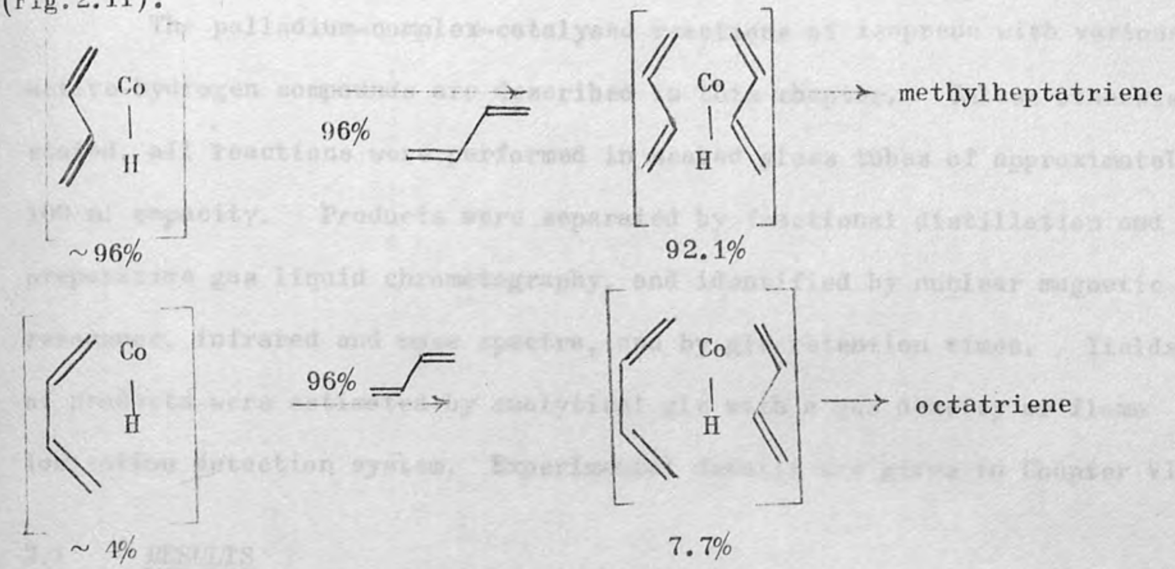


Fig.2.11

The reaction of isoprene with a catalyst consisting of cobalt chloride, sodium borohydride and triphenylphosphine in ethanol has been investigated(41). With a P/Co ratio of less than one, 2,3,5-trimethyl-1,4,6-heptatriene was the main product. At P/Co ratios above one, 2,7-dimethyl-1,trans-3, 7-octatriene and 2,6-dimethyl-1, trans 3,6-octatriene were obtained. In aprotic solvents such as toluene, 2,4-dimethyl-4-vinyl-1-cyclohexene and dipentene were the only products.

CHAPTER III

PALLADIUM-CATALYSED REACTIONS OF ISOPRENE

The palladium-complex-catalysed reactions of isoprene with various active-hydrogen compounds are described in this chapter. Unless otherwise stated, all reactions were performed in sealed glass tubes of approximately 100 ml capacity. Products were separated by fractional distillation and preparative gas liquid chromatography, and identified by nuclear magnetic resonance, infrared and mass spectra, and by glc retention times. Yields of products were estimated by analytical glc with a gas density or flame ionization detection system. Experimental details are given in Chapter VI.

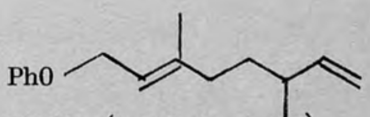
3.1 RESULTS

3.1.1 Telomerisation of Isoprene with Phenol

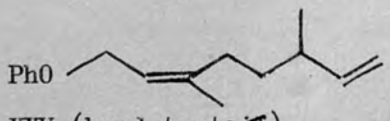
The telomerisation of isoprene with phenol in the presence of several palladium catalyst systems was studied. The results are summarised in Table 3.1. In all these reactions the quantities of reactants were:

palladium catalyst	:	0.1 mMole
cocatalyst	:	0.1 mMole
phenol	:	0.1 Mole
isoprene	:	0.3 Mole
solvent (benzene)	:	20 cm^3

Four phenyl isoprene-dimer ethers (XXIV - XXVII) were identified as products of these reactions; a fifth ether was tentatively assigned the structure XXVIII, although the nmr integration was not entirely consistent with this.



XXIV (head-to-~~tail~~) head

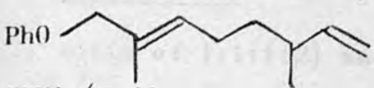


XXV (head-to-~~tail~~) head

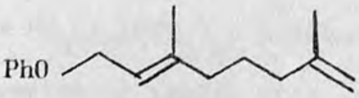
TABLE 3.1

THE PALLADIUM CATALYSED REACTION OF ISOPRENE WITH PHENOL

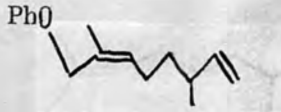
Expt. No.	Catalyst	Conditions	Phenol Conversion (%)	PRODUCT DISTRIBUTION		DISTRIBUTION OF ETHERS (%)				
				% Trienes	% Ethers	XXIV	XXV	XXVI	XXVII	XXVIII
Pd/26	$PdCl_2(PPh_3)_2$ - NaOPh	25°/24h	trace	-	-	trace	-	-	-	-
Pd/27	$PdCl_2(PPh_3)_2$ - NaOPh	85°/24h	40	27	73	63	12	21	1	3
Pd/28	$(\pi\text{-}C_3H_5)_2Pd_2Cl_2$ - NaOPh	0°/24h	trace	-	-	trace	-	-	-	-
Pd/29	$(\pi\text{-}C_3H_5)_2Pd_2Cl_2$ - NaOPh	25°/24h	trace	-	-	trace	-	-	-	-
Pd/32	$(\pi\text{-}C_3H_5)_2Pd_2Cl_2$-NaOPh-$PPh_3$	85°/24h	86	18	82	33	6	49	4,5	7,5
Pd/44	$Ph_3Cl_4(PPh_3)_2$ - NaOPh	85°/24h	-	-	-	-	-	-	-	-
Pd/34	$(\pi\text{-}C_3H_5)_2Pd_2Cl_2$-NaOPh-$PBu_3$	85°/24h	69	6	94	74,5	15	7	0,5	3
Pd/41	$PdCl_2(PBu_3)_2$ - NaOPh	85°/24h	trace	-	-	trace	-	-	-	-
Pd/43	$PdCl_2(Pcy_3)_2$ - NaOPh	85°/24h	20	0	100	87	-	13	-	-



XXVI (tail-to-head)



XXVII (head-to-tail)



XXVIII (tail-to-head)

The ratios of these products could be varied to some extent by the use of different catalyst systems, and the head-to-head dimer (XXIV or the tail-to-head dimer XXVI could be made the major product.

(a) Catalyst systems containing no phosphine ligands (Expts. Pd/28, Pd/29)

Although the system (π-allyl) palladium chloride-sodium phenoxide has been reported to give high yields of phenyl ethers(39) and to remain homogeneous, our experience was that decomposition to palladium metal usually occurred to a considerable extent above -5° to 0°. It appears that it is necessary to raise the temperature of the reaction mixture very slowly from about -10° to avoid decomposition. In one case this was achieved, and the head-to-head dimer XXIV was the major product. In Expts. Pd/28 and Pd/29, decomposition was considerable, and only traces of XXIV was obtained.

(b) Catalyst systems containing triphenylphosphine ligands (Expts Pd/26, Pd/27, Pd/32, Pd/44)

Expt. Pd/32. The system π-allyl palladium chloride-sodium phenoxide-triphenylphosphine (Pd : base : ligand : Cl ratio of 1:1:1:1) was the most efficient of all the systems investigated, giving, after 24 hours at 85°, an 86% conversion of phenol, and the tail-to-head dimer XXVI as major product (49%).

Expt. Pd/27. The $PdCl_2(PPh_3)_2$ - sodium phenoxide system (Pd : base : ligand : Cl ratio of 1:1:2:2) was far less active (40% conversion of phenol after 24 hours at 85°) but in this case the head-to-head dimer XXIV was the major product (63%). At 25° this system gave traces only of XXIV (Expt. Pd/26).

Expt. Pd/44. The system $Pd_2Cl_4(PPh_3)_2$ - sodium phenoxide (Pd:base:ligand:Cl ratio of 1:1:1:2) was completely ineffective.

(c) Catalyst systems containing other ligands
(Expts. Pd/41, Pd/34, Pd/43)

Expt.Pd/41. The system $PdCl_2(P\ Bu_3)_2$ - sodium phenoxide (Pd:base:ligand:Cl ratio of 1:1:2:2) at 85° proved inactive, giving traces of XXIV as the only product.

Expt. Pd/34. The system π-allyl palladium chloride - sodium phenoxide - tributylphosphine (Pd:base:ligand:Cl ratio of 1:1:1:1) at 85° gave a 69% conversion of phenol, the major product being the head-to-head dimer XXIV (74.5%).

Expt. Pd/43. The system $PdCl_2(P\ Cy_3)_2$ - sodium phenoxide (Pd:base:ligand:Cl ratio of 1:1:2:2) at 85° gave a 20% conversion of phenol to XXIV (87%) and XXVI (13%). No trienes were obtained in this reaction.

Expt. Pd/19. The phenyl ethers XXIV - XXVIII can, under suitable conditions, be degraded to phenol and trienes. Treatment of a mixture of the phenyl ethers with a π-allyl palladium chloride-triphenylphosphine-sodium-phenoxide catalyst under reduced pressure (0.1 mm Hg) gave a 94% yield of phenol and trienes, which distilled into a cold-trap as they were formed. The structures of the trienes and their presumed origins are shown in Fig.3.1.

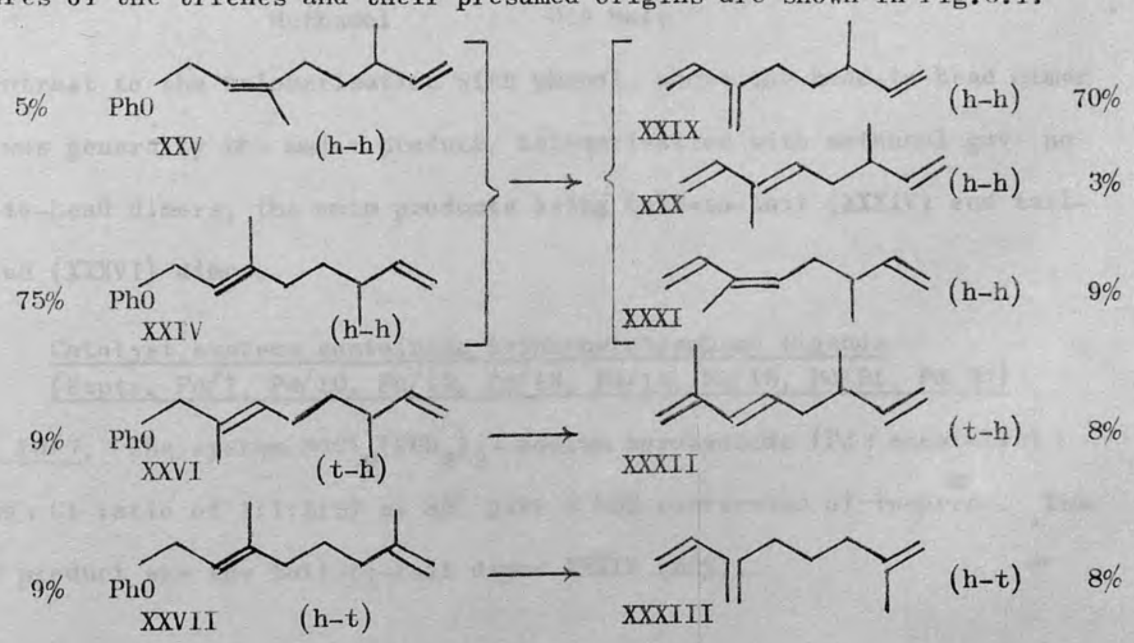
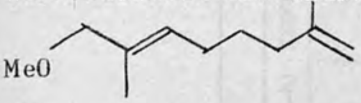


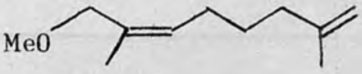
Fig.3.1

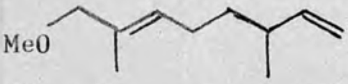
3.1.2 Telomerisation of Isoprene with Methanol and other Alcohols

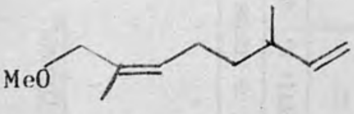
METHANOL

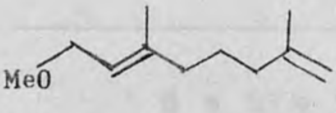
In the telomerisation of isoprene with methanol, a wider range of ethers was obtained than was the case with phenol. Seven ethers (XXXV - XL) were isolated and characterised.

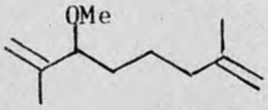

XXXIV (tail-to-tail)

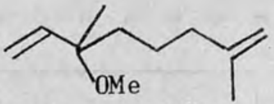

XXXV (tail-to-tail)


XXXVI (tail-to-head)


XXXVII (tail-to-head)


XXXVIII (head-to-tail)


XXXIX (tail-to-tail)


XL (head-to-tail)

The results of experiments with various catalyst systems are given in Table 3.2. In all cases the quantities of reactants were:

Pd catalyst	:	0.5 mMole
Cocatalyst	:	0.5 mMole (where relevant)
Phosphine	:	0.5 mMole
Isoprene	:	0.5 Mole
Methanol	:	0.5 Mole

In contrast to the telomerisation with phenol, where the head-to-head dimer XXIV was generally the major product, telomerisation with methanol gave no head-to-head dimers, the main products being tail-to-tail (XXXIV) and tail-to-head (XXXVI) dimers.

(a) Catalyst systems containing triphenylphosphine ligands (Expts. Pd/7, Pd/10, Pd/12, Pd/13, Pd/14, Pd/15, Pd/31, Pd/37)

Expt. Pd/7. The system PdCl$_2$(PPh$_3$)$_2$ - sodium borohydride (Pd : cocatalyst : ligand : Cl ratio of 1:1:2:2) at 85° gave a 63% conversion of isoprene. The major product was the tail-to-tail dimer XXXIV (52%).

TABLE 3.2

THE PALLADIUM-CATALYSED REACTION OF ISOPRENE WITH METHANOL

Expt. No.	Catalyst System	Conditions	Isoprene Conversion	PRODUCT DISTRIBUTION		DISTRIBUTION OF ETHERS (%)						
				% Trienes	% Ethers	XXXIV(t-t)	XXXV(t-t)	XXXVI(t-h)	XXXVII(t-h)	XXXVIII(h-t)	XXXIX(t-t)	XL(h-t)
Pd/7	$PdCl_2(PPh_3)_2$-$NaBH_4$	85°/24h	63	19	81	52	9	22	2	3	9	3
Pd/8	$PdCl_2(PBu_3)_2$-$NaBH_4$	85°/24h	38	33	67	26	5	52	10	1	6	1
Pd/10	$PdCl_2(PPh_3)_2$-$NaBH_4$	25°/24h	7,5	9	91	17	<1	70	9	1	2	<1
Pd/11	$PdCl_2(PBu_3)_2$-$NaBH_4$	25°/24h	-	-	-	-	-	-	-	-	-	-
Pd/12	$Pd_2Cl_4(PPh_3)_2$-$NaBH_4$	85°/24h	-	-	-	-	-	-	-	-	-	-
Pd/13	$PdCl_2(PPh_3)_2$-Et_3N	85°/24h	-	-	-	-	-	-	-	-	-	-
Pd/14	$PdCl_2(PPh_3)_2$-NaOPh	85°/24h	73	27	73	61	3	25	1	3	5	2
Pd/15	$Pd(PPh_3)_4$	85°/24h	69	12	88	60	1	26	1	3	5	4
Pd/25	$PdCl_2(Pcy_3)_2$-NaOPh	85°/24h	9	16	84	12	2	67	16	1	1	1
Pd/31	$(\pi\text{-}C_3H_5)_2Pd_2Cl_2$-$PPh_3$-NaOPh	85°/24h	88	33	67	56	6	27	1	2	6	2
Pd/36	$Pd(acac)_2$ - $P(OPh)_3$	85°/24h	84	62	38	51	3	40	5	-	-	1
Pd/37	$Pd(acac)_2$ - PPh_3	85°/24h	84	59	41	52	4	34	4	-	6	-

Expt. Pd/10. At 25° the above system gave a 7.4% conversion of isoprene, and the major product was the tail-to-head dimer XXXVI (70%).

Expt. Pd/12. The system $Pd_2Cl_4(PPh_3)_2 - NaBH_4$ (Pd : cocatalyst : ligand : Cl ratio of 1:1:1:2) at 85° was completely inactive.

Expt. Pd/13. The system $PdCl_2(PPh_3)_2 - Et_3N$ (Pd : cocatalyst : ligand : Cl ratio of 1:1:2:2) at 85° was completely inactive.

Expt. Pd/14. The system $PdCl_2(PPh_3)_2 - NaOPh$ (Pd : cocatalyst : Ligand : Cl ratio of 1:1:2:2) at 85° gave a 73% conversion of isoprene. The major product was the tail-to-tail dimer XXXIV (61%).

Expt. Pd/15. The system $Pd(PPh_3)_4$ at 85° gave a 69% conversion of isoprene. The major product was again XXXIV (60%).

Expt. Pd/31. The system $(\pi\text{-}C_3H_5)_2Pd_2Cl_2 - NaOPh - PPh_3$ (Pd : cocatalyst : ligand : Cl ratio of 1:1:1:1) at 85° gave an 88% conversion of isoprene; the major product was again XXXIV (56%).

Expt. Pd/37. The system $Pd(acac)_2 - PPh_3$ (Pd : cocatalyst : ligand : Cl ratio of 1:0:1:0) at 85° gave an 84% conversion of isoprene. The tail-to-tail dimer XXXIV was the major other product.

(b) Catalyst systems containing other ligands (Expts. Pd/8, Pd/11, Pd/25, Pd/36)

Expt. Pd/8. The system $PdCl_2(P\ Bu_3)_2 - NaBH_4$ (Pd : cocatalyst : ligand : Cl ratio of 1:1:2:2) at 85° gave a 38% conversion of isoprene; the major product was the tail-to-head dimer XXXVI (52%).

Expt. Pd/11. The above system at 25° was inactive; no products were detected by glc.

Expt. Pd/25. The system $PdCl_2(PCy_3)_2 - NaOPh$ (Pd : cocatalyst : ligand : Cl ratio of 1:1:2:2) at 85° gave a 9% conversion of isoprene. The major product was XXXVI (67%).

Expt. Pd/36. The system Pd(acac)$_2$ - P(OPh)$_3$ (Pd : cocatalyst : Ligand : Cl ratio of 1:0:1:0) at 85° gave an 84% conversion of isoprene; the major ether product was XXXIV (52%).

An attempt was made to ascertain whether the C_{10} chain formed by the dimerisation of isoprene could subsequently be broken by a palladium catalyst. If this were so, heating a mixture of methyl isoprene-dimer ethers in the presence of a palladium catalyst might result in some re-arrangement of the ethers. This was tested using two mixtures of ethers, one of which consisted mainly of XXXVI and the other of XXXIV.

Expt. Pd/18a. The mixture of ethers obtained from Expt. Pd/10 was heated at 85° for 24 hours with the PdCl$_2$(PPh$_3$)$_2$ - NaOPh catalyst in methanol solution. The ratios of the various ethers were then re-measured. No trienes were formed in the reaction.

Expts. Pd/18b and Pd/18c. The mixture of ethers obtained from Expt. Pd/15 was heated at 85° for 24 hours with the PdCl$_2$(PPh$_3$)$_2$ - NaOPh catalyst in methanol solution (Expt.Pd/18b) and benzene solution (Expt. Pd/18c). The ratios of the products were then re-measured.

The results of these three experiments are given in Table 3.3 (ratios before reaction are given in parentheses).

TABLE 3.3

RESULTS OF EXPTS. Pd/18a, 18b, 18c

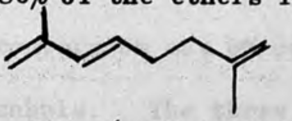
Expt. No.	DISTRIBUTION OF ETHERS (%)						
	XXXIV	XXXV	XXXVI	XXXVII	XXXVIII	XXXIX	XL
Pd/18a	17 (17)	0 (<1)	70 (70)	9 (9)	1 (1)	2 (2)	1 (<1)
Pd/18b	60 (60)	2 (1)	25 (27)	2 (3)	3 (2)	5 (4)	3 (3)
Pd/18c	61 (60)	2 (1)	27 (27)	1 (3)	2 (2)	4 (4)	3 (3)

It may be seen that no significant re-arrangement occurred. This would suggest that once the C_{10} chain is formed, it will not break up under these conditions.

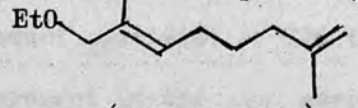
OTHER ALCOHOLS

Expt. Pd/16 - Ethanol

The system $Pd(PPh_3)_4$ telomerised isoprene and ethanol at 85° with an isoprene conversion of 44%. The major products were the triene XLI (tail-to-tail) and the ether XLII (also tail-to-tail); the latter constituted 80% of the ethers formed. Trienes were 21% of the product, ethers 79%.



XLI (tail-to-tail)



XLII (tail-to-tail)

Expt. Pd/22 - n-Propanol

The system $PdCl_2(PPh_3)_2$ - NaOPh (Pd : cocatalyst : ligand : Cl ratio of 1:1:2:2) at 85° gave a 25% conversion of isoprene. Trienes constituted 73% of the product and ethers 27%. The major triene (> 85% of the triene fraction) was identified by glc retention time as XLI. The major ether was assumed to be the n-propoxy analogue of XLII.

Expt. Pd/24 - iso-Propanol

The system $PdCl_2(PPh_3)_2$ - NaOPh (Pd : cocatalyst : ligand : Cl ratio of 1:1:2:2) at 85° was inactive. Very small amounts of cyclic dimers (thermally formed) were the only product.

Expt. Pd/23 - tert-Butanol

The system $PdCl_2(PPh_3)_2$ - NaOPh (Pd : cocatalyst : ligand : Cl ratio of 1:1:2:2) at 85° was inactive. Thermal dimers were the only products.

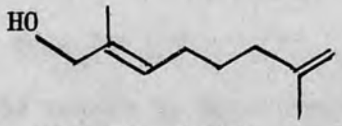
3.1.3 The Telomerisation of Isoprene with Water

The presence of carbon dioxide has been reported to facilitate the palladium-catalysed telomerisation of butadiene with water(73) to give 1-hydroxy-octadienes. Accordingly the telomerisation of isoprene with water was attempted.

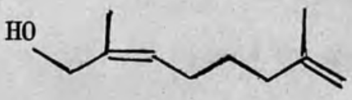
Expt. Pd/38

Isoprene (2 Mole), water (2 Mole), acetone (100 ml), palladium acetylacetonate (1 mMole) and triphenylphosphine (3 mMole) were placed in a 400 ml Teflon-lined autoclave equipped with a stirrer. Carbon dioxide was introduced to approximately 50 p.s.i. and the autoclclave was heated at 95° for 18 hours. Considerable decomposition to palladium metal occurred. Isoprene conversion was 6% only, and the product consisted of 92% trienes and 8% alcohols. The three alcohol peaks present in the glc were separated by preparative glc. The mass spectra of all three compounnds had a parent ion at m+/e 154. The n m r spectrum of the major alcohol formed was not interpretable, but the others were assigned the structures LXVIII and LXIX. They were formed in the proportions shown.

unknown
(63%)



LXVIII (28%)



LXIX (9%)

3.2 DISCUSSION

We have shown that palladium-catalysed telomerisation of isoprene may yield predominantly head-to-head, tail-to-head or tail-to-tail products. Head-to-head major products were formed in most cases when isoprene was telomerised with phenol, but in the case of the π-allyl palladium chloride-sodium phenoxide-triphenylphosphine catalyst system, the major product was the tail-to-head dimer XXVI.

Isoprene-methanol telomerisation offered a strong contrast, in that head-to-head dimers were not obtained at all; the major product was either the tail-to-tail dimer XXXIV or the tail-to-head dimer XXXVI, depending on the ligand and temperature used.

From the evidence of Expts. Pd/18a, 18b and 18c it seems unlikely that there is any interconversion of the various ethers with C_{10} skeletons once they are formed. Thus thermodynamic control of the product distribution may probably be ruled out in favour of kinetic controls, which have their origin in the properties of the intermediate organometallic complexes.

The literature contains few references to palladium-catalysed isoprene dimerisation. Smutny et al(39) obtained head-to-head phenyl ether as major product from the reaction of isoprene and phenol using a π-allyl palladium chloride-sodium phenoxide catalyst. Suga et al(68) telomerised isoprene with acetic acid using a $PdCl_2$-NaOAc catalyst to give a mixture of head-to-head, tail-to-head and head-to-tail acetates. Isoprene and active methylene compounds in the presence of the $PdCl_2(PPh_3)_2$ - NaOPh catalyst gave products having almost exclusively the tail-to-tail structure(121). Recently it has been reported(151) that isoprene was oligomerised in the presence of $PdBr_2(Ph_2PCH_2CH_2PPh_2)_2$ - NaOPh and phenol to give five linear dimers. The ratios in which these dimers were produced was found to depend on the phenol-isoprene ratio. At a ratio of 1:30 the major product was the tail-to-tail dimer 2,7-dimethyl- 1,trans - 3,7-octatriene, while at a ratio of 1:15, the head-to-head dimers 2-vinyl - 5 - methyl - 1,6-heptadiene (XXIX) and 3,6-dimethyl-1, cis-3, 7 octatriene XXXI were the major products. At a phenol-isoprene ratio of 1:3, the head-to-tail dimer 2,6-dimethyl-1,trans 3,7 octatriene XXXII was obtained. All these products except the first, 2,7-dimethyl-1, trans-3, 7-octatriene, have been identified by us as being formed in the degradation of phenyl isoprene-dimer ethers to phenol and isoprene. In fact, a tail-to-tail phenyl ether was not observed by us in any of our reactions (in all of which the phenol: isoprene ratio was 1:3).

In the case of isoprene-methanol telomerisation it is noteworthy that all those systems containing PPh_3 as ligand at 85° gave essentially the same distribution of products. This suggests strongly that a common catalytic intermediate may be formed, whatever the starting materials.

As $Pd(PPh_3)_4$ and $Pd(acac)_2$-PPh_3 gave similar results to the $PdCl_2(PPh_3)_2$-NaOPh system, the active catalytic species probably does not contain phenoxide ligands; if it does, they seem to exert no influence on the course of the reaction. The role of the sodium phenoxide is probably to remove chloro ligands from the palladium complex, leaving weakly bonded phenoxide ligands, which may readily be displaced by isoprene. Sodium borohydride seems to act in the same manner. Interestingly, the chloro-bridged complex $Pd_2Cl_4(PPh_3)_2$ with sodium phenoxide or sodium borohydride was completely inactive in the telomerisation of isoprene with methanol or phenol. The reason for this is not clear.

There appears to be some correlation between the base strength of the phosphine ligand used and the nature of the products formed from the isoprene-methanol telomerisation. The stronger σ-donors (and weaker π-acceptors) such as PBu_3 and Pcy_3 seemed to favour tail-to-head dimerisation, while PPh_3 gave mainly tail-to-tail products and $P(OPh)_3$ occupied an intermediate position, as would be expected for a σ-donor-strength order of

$$PBu_3 \simeq Pcy_3 > P(OPh)_3 > PPh_3$$

In addition, systems containing PBu_3 or Pcy_3 as ligand seemed to give generally lower conversions of isoprene than those containing PPh_3. It seems likely that the efficiency of the catalyst is reduced by the stronger Pd-P coordination in the case of the alkylphosphines. Indeed, the $PdCl_2(PBu_3)_2$-NaOPh system was inactive for telomerisation of isoprene with phenol.

The isoprene-phenol telomerisation gave the head-to-head dimer XXIV as major product in all cases but one : the (π-allyl) palladium chloride-sodium phenoxide-triphenyphosphine system gave the tail-to-head dimer as the major constituent of the ether fraction (49%), and also gave the highest phenol conversion (86%). This anomalous result was confirmed on repetition of the experiment, and suggests that the ratio of palladium to phosphine may have an influence on the product distribution.

The ease with which the phenyl isoprene-dimer ethers could be degraded to phenol and trienes provides support for our belief that there exists an equilibrium in the reactive mixture between trienes and ethers:

$$ROC_{10}H_{17} \rightleftharpoons ROH + C_{10}H_{16} \quad (R = Ph,\ Me\ etc.)$$

This equilibrium was found to be at very different points, depending on the catalyst system used. The reasons for this are not understood.

Literature reports previous to this work had shown that the dimerisation of isoprene was affected by the nature of the nucleophilic species present. We have confirmed that this is so, and have shown that the nature of the ligands, the metal-to-ligand ratio and the temperature at which the reaction is performed can also affect the distribution of the products.

CHAPTER IV

NICKEL-CATALYSED REACTIONS OF ISOPRENE

This Chapter describes the nickel-catalysed reaction of isoprene with active-hydrogen compounds. All reactions were performed in sealed glass tubes of approximately 100 ml capacity. Products were separated by fractional distillation and preparative glc and identified by nuclear magnetic resonance, infra red and mass spectrometry, and by glc retention times. Yields were estimated by glc. Experimental details are given in Chapter VI.

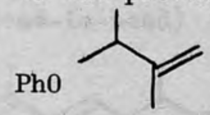
4.1 RESULTS

4.1.1 Telomerisation of Isoprene with Phenol

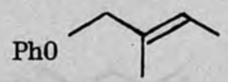
The reaction of isoprene with phenol in the presence of two zero-valent nickel phosphite complexes was studied.

Expt. Ni/34 - $Ni[P(OEt)_3]_4$

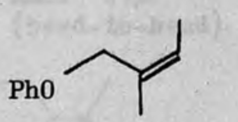
$Ni[P(OEt)_3]_4$ (1.0 mMole), isoprene (0.5 Mole) and phenol (0.1 Mole) were heated at 85° for 24 hours. A 10% conversion of phenol was obtained to the products XLVI - L formed in the ratios shown:



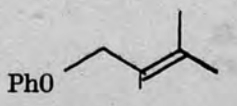
XLVI 56%



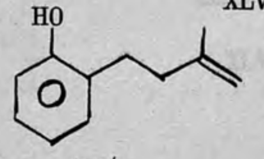
XLVII 3%



XLVIII 7%



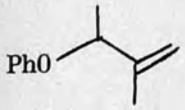
XLIX 9%



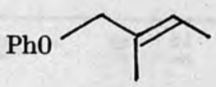
L 17%

Expt. Ni/35 - $Ni[P(OPh)_3]_4$

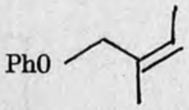
$Ni[P(OPh)_3]_4$ (1.0 mMole), isoprene (0.5 Mole) and phenol (0.1 Mole) were heated at 85° for 24 hours. Phenol conversion was 41%. The major product was the ether XLVI. Phenyl isoprene-dimer ethers were also formed in small amounts.



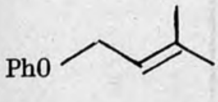
XLVI 64%



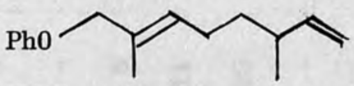
XLVII 4%



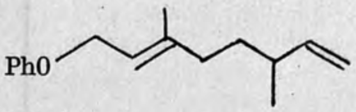
XLVIII 7%



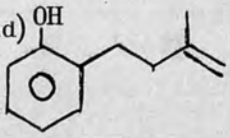
XLIX 14%



XXVI 2%
(tail-to-head)



XXIV 5%
(head-to-head)



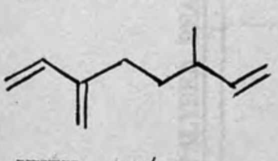
L 5%

4.1.2 Telomerisation of Isoprene with Methanol

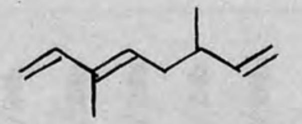
The reaction of isoprene and methanol was studied in the presence of several nickel complexes. The results are summarised in Table 4.1.

Expt. Ni/21 - $Ni(H)(BH_4)(Pcy_3)_2$

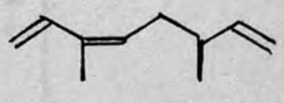
$Ni(H)(BH_4)(Pcy_3)_2$ (0.5 mMole), isoprene (0.5 Mole) and methanol (0.5 Mole) were heated for 24 hours at 85°. Isoprene conversion was 6.5%, to a mixture of dimers as shown:



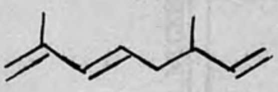
XXIX 13%
(head-to-head)



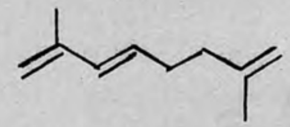
XXX 27%
(head-to-head)



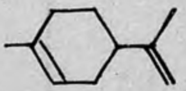
XXXI 17%
(head-to-head)



XXXII 18%
(tail-to-head)



XLI 9%
(tail-to-tail)



XLV 16%

Expt. Ni/22 - $Ni(H)Cl(Pcy_3)_2$

$Ni(H)Cl(Pcy_3)_2$ (0.5 mMole), isoprene (0.5 Mole) and methanol (0.5 Mole) were heated at 85° for 24 hours. Glc analysis revealed no products other than very small amounts of thermal dimers, principally XLV.

TABLE 4.1

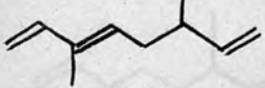
THE NICKEL-CATALYSED REACTION OF ISOPRENE WITH METHANOL

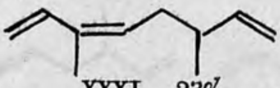
		Conditions	Conversion of Isoprene (%)	DISTRIBUTION OF PRODUCTS (%)							
				XXIX	XXX	XXXI	XXXII	XLI	XLIII	XLIV	XLV
Ni/21	$Ni(H)(BH_4)(Pcy_3)_2$	85°/24h	6,5	13	27	17	18	9	–	–	16
Ni/22	$Ni(H)Cl(Pcy_3)_2$	85°/24h	*	–	–	–	–	–	–	–	*
Ni/27	$Ni(CH_2CHCN)_2 - PBu_3$	85°/24h	18	–	29	23	9	11	6	–	16
Ni/28	$Ni(CH_2CHCN)_2 - PPh_3$	85°/24h	15	–	12	19	11	14	11	14	12
Ni/29	$Ni(CH_2CHCN)_2 - P(OEt)_3$	85°/24h	3,5	2	2	2	1	21	20	14	28
Ni/31	$NiCl_2 - PhP(O^iPr)_2 - NaBH_4$	85°/24h	*	–	–	–	–	–	–	–	*
Ni/32	$Ni(acac)_2 - PhP(O^iPr)_2 - NaBH_4$	85°/24h	<1%	33	11	–	–	21	–	–	53

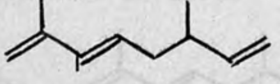
* Not Determined

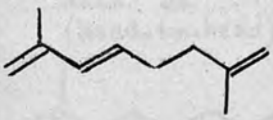
Expt. Ni/27 - Ni(CH_2=CHCN)$_2$ - PBu_3

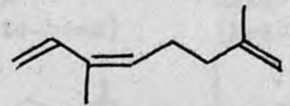
Ni(CH_2=CHCN)$_2$ (0.59 mMole), PBu_3 (0.59 mMole, isoprene (0.5 Mole) and methanol (0.5 Mole) were heated at 85° for 24 hours. Isoprene conversion was 18%, to a mixture of dimers in the proportions shown:

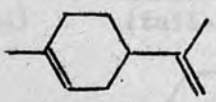

XXX 29%
(head-to-head)


XXXI 23%
(head-to-head)


XXXII 9%
(tail-to-head)

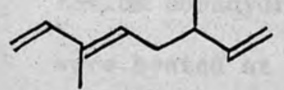

XLI 11%
(tail-to-tail)

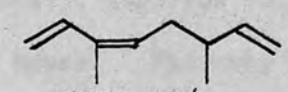

XLIII 6%
(head-to-tail)

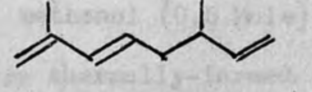

XLV 16%

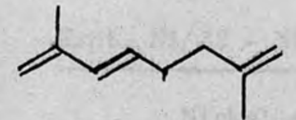
Expt. Ni/28 - Ni(CH_2=CHCN)$_2$ - PPh_3

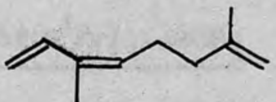
Ni(CH_2=CHCN)$_2$ (0.74 mMole), PPh_3 (0.74 mMole) isoprene (0.5 Mole) and methanol (0.5 Mole) were heated at 85° for 24 hours. A 15% conversion of isoprene was obtained to a mixture of dimers:

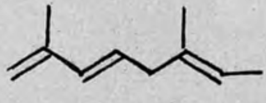

XXX 12%
(head-to-head)

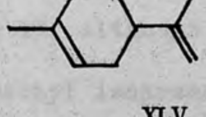

XXXI 19%
(head-to-head)


XXXII 11%
(tail-to-head)


XLI 14%
(tail-to-tail)


XLIII 11%
(head-to-tail)

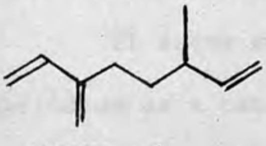

XLIV 14%
(tail-to-head)

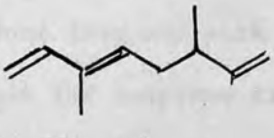

XLV 12%

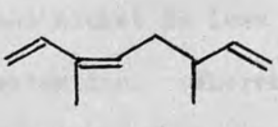
unidentified 7%

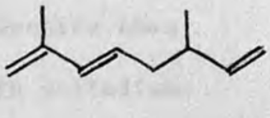
Expt. Ni/29 - $Ni(CH_2{=}CHCN)_2 - P(OEt)_3$

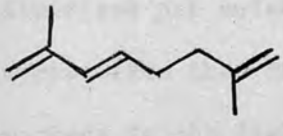
$Ni(CH_2CHCN)_2$ (0.825 mMole), $P(OEt)_3$ (0.825 mMole), isoprene (0.5 Mole) and methanol (0.5 Mole) were heated at 85° for 24 hours. Isoprene conversion was 3.5%. The product distribution was as shown:

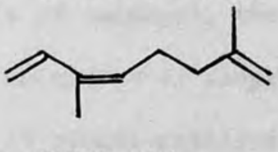

XXIX 2%
(head-to-head)

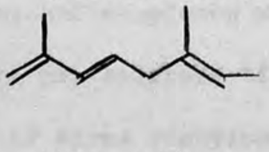

XXX 2%
(head-to-head)

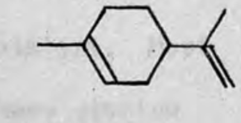

XXXI 2%
(head-to-head)


XXXII 1%
(tail-to-head)


XLI 21%
(tail-to-tail)


XLIII 20%
(head-to-tail)


XLIV 14%
(tail-to-head)


XLV 28%

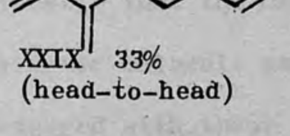
unidentified 10%

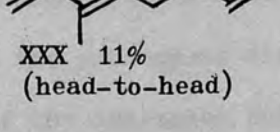
Expt. Ni/31 - $NiCl_2 - PhP(O^iPr)_2 - NaBH_4$

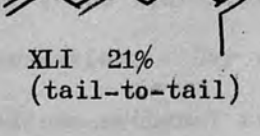
Nickel chloride (0.5 mMole), phenyldiisopropoxyphosphine (0.75 mMole), sodium borohydride (0.1 mMole), isoprene (0.5 Mole) and methanol (0.5 Mole) were heated at 85° for 24 hours. The only products were thermally-formed cyclodimers.

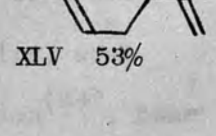
Expt. Ni/32 - $Ni(acac)_2 - PhP(O^iPr)_2 - NaBH_4$

Nickel acetylacetonate (1.0 mMole), phenyldiisopropoxyphosphine (1.5 mMole) sodium borohydride (0.016 g), isoprene (0.5 Mole) and methanol (0.5 Mole) were heated at 85° for 24 hours. Conversion of isoprene to dimers was less than 1%, although considerable conversion to lower-boiling products (probably methyl isoprene monomer ethers) occurred. The composition of the dimer fraction was as shown:


XXIX 33%
(head-to-head)


XXX 11%
(head-to-head)


XLI 21%
(tail-to-tail)


XLV 53%

Traces of methyl isoprene-dimer ethers were also obtained, but their glc retention times did not correspond with any of those obtained from palladium-catalysed reactions.

4.2 DISCUSSION

It seems evident from our work that nickel is less effective than palladium as a catalyst for isoprene dimerisation. Whereas in palladium-catalysed reactions at least 800-950 molecules of isoprene could be dimerised per molecule of catalyst, the nickel complexes we studied converted less than 200 molecules of isoprene per molecule of catalyst. Most workers in the field of nickel catalysis of diene reactions have studied butadiene rather than isoprene, but there is some evidence to suggest that isoprene is considerably more sluggish in its reactions than in butadiene. For example, in the cyclotrimerisations of butadiene and isoprene by nickel catelysts(83), it was found that butadiene reacted approximately 20 times faster than isoprene under the same conditions. It has also been reported that increasing methyl-substitution on butadiene slows the rate of the nickel-catalysed reaction with active methylene compounds(56). This difference in behaviour of the methyl-substituted dienes may be due to increased stability of the π-allylic intermediates.

Of the catalysts we used for the dimerisation of isoprene in methanol, $Ni(H)(BH_4)(Pcy_3)_2$ and the nickel acrylonitrile-phosphine or phosphite systems were most efficient, the former being much easier to handle. The nickel acetylacetonate-phenyldiisopropoxyphosphine-sodium borohydride system was very inefficient for dimer formation, but was peculiar in that methyl isoprene-monomer ethers were obtained in reasonable conversion. It seems probable that the chelating ligand acac-prevents coordination of a second isoprene molecule and the subsequent dimerisation. Our results, when compared with those of the analogous butadiene-methanol reaction(54), bear out the observation of Baker et al(57) that methyl-substituted butadienes not only react more slowly than does butadiene itself, but also give a greater proportion of monomeric products.

Interestingly, both catalyst systems containing halide - $NiCl_2 - PhP(O^iPr)_2 - NaBH_4$ and $Ni(H)Cl(Pcy_3)_2$ - were completely inactive for the formation of linear dimers. This contrasts with the recent report(57) that in the reaction of butadiene with active methylene complexes such as benzyl methyl ketone, the order of reactivity of catalysts was

$$NiBr_2 \simeq NiCl_2 > Ni(acac)_2 > Ni(acetate)_2 > Ni(laurate)_2$$

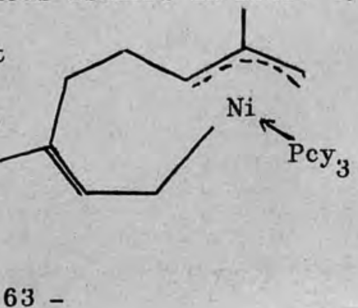
The nickel catalyst systems studied by us were very unselective, giving a mixture of $C_{10}H_{16}$ isomers which was rather difficult to separate. Head-to-head isomers predominated (31 - 57% of the linear dimers formed) except in the case of the $Ni(CH_2CHCN)_2 - P(OEt)_3$ system, where they were present only to the extent of 6%. In the latter case head-to-tail dimer XLIII (trans-α-ocimene) constituted 20% of the product. The proportions of the various type of isomer are summarised in Table 4.2.

TABLE 4.2

DISTRIBUTION OF LINEAR DIMERS IN NICKEL-CATALYSED REACTIONS

Expt. No.	% OF DIMERIC PRODUCT			
	head-to-head	tail-to-tail	tail-to-head	head-to-tail
Ni/21	57	9	18	-
Ni/27	52	11	9	6
Ni/28	31	14	25	11
Ni/29	6	21	15	20
Ni/32	44	21	-	-

The distribution of the various isomers in Table 4.2 is interesting in view of the fact that Barnett et al(140) isolated the complex VII, where the methyl groups are in the



VII

2,6 positions. Evidently under our reaction conditions complexes having the methyl groups in other positions are also formed.

It appears unlikely from our results that nickel-catalysed oligomerisation of isoprene will be a useful source of terpenoid compounds unless a catalyst can be found which is both more efficient and more selective for head-to-tail dimers.

CHAPTER V

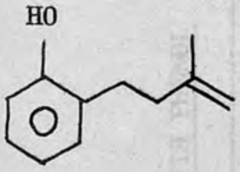
RHODIUM-CATALYSED REACTIONS OF BUTADIENE AND ISOPRENE

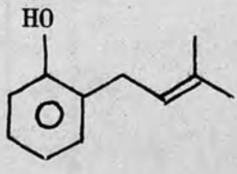
Rhodium-complex-catalysed reactions of isoprene and butadiene are described in this chapter. Experimental details are given in Chapter VI.

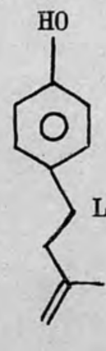
5.1 RESULTS

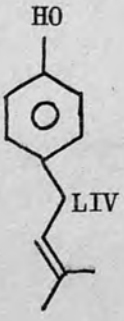
5.1.1 Reaction of Isoprene with Phenol

The reaction of isoprene with phenol was studied in the presence of several rhodium complexes, with and without sodium phenoxide cocatalyst. Only one complex, $\mathrm{RhCl(PPh_3)_3}$, was found to be active. Products were the substituted phenols, L, LII - LV. Traces of lower-boiling products (assumed to be phenyl monomer ethers from their glc retention times) were also obtained, but were not investigated. No phenyl-isoprene dimer ethers were produced. The substituted phenols were all isolated by distillation and preparative glc, and characterised by nuclear magnetic resonance, infrared and mass spectroscopy. The presence of both $\mathrm{RhCl(PPh_3)_3}$ and the cocatalyst sodium phenoxide was shown to be essential; in the absence of either, no reaction occurred. The reaction also failed when anisole was substituted for phenol. The results are summarised in Table 5.1.


L


LII


LIII


LIV

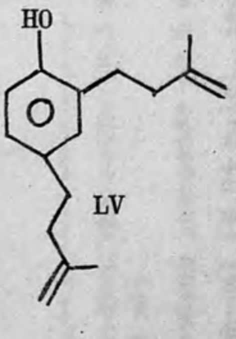

LV

TABLE 5.1

THE REACTION OF ISOPRENE WITH PHENOL

Expt. No.	Catalysts	Conditions	Phenol Conversion (%)	PRODUCT DISTRIBUTION (%)				
				L	LII	LIII	LIV	LV
Rh/6	$RhCl(PPh_3)_3$ NaOPh	85°/24h	18	47	10	40	3	trace
Rh/16	NaOPh	85°/24h	–	–	–	–	–	–
Rh/20	$RhCl(PPh_3)_3$	85°/24h	–	–	–	–	–	–
Rh/12	$RhCl(PPh_3)_3$ NaOPh	85°/24h	23	58	9	28	2	3
Rh/7	$Rh(nbd)_2^+BF_4^-$ NaOPh	85°/24h	–	–	–	–	–	–
Rh/8	$RhCl_3-3H_2O$ NaOPh	85°/24h	–	–	–	–	–	–
Rh/18	$RhCl_2(Pcy_3)_2$ NaOPh	85°/24h	–	–	–	–	–	–

All reactions: Rhodium catalyst (0.5 mMole), sodium phenoxide (0.5 mMole), phenol (0.2 Mole), isoprene (0.1 Mole), benzene (35 ml).

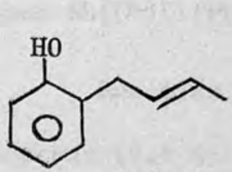
except Rh/12: Rhodium catalyst (0.5 mMole), sodium phenoxide (0.5 mMole), phenol (0.1 Mole), isoprene (0.5 Mole)

Rh/16: Sodium phenoxide (0.1 mMole), phenol (0.04 Mole), isoprene (0.02 Mole), benzene (10 ml)

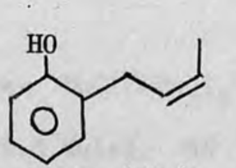
Rh/20: Rhodium catalyst (0.1 mMole), phenol (0.04 Mole), isoprene (0.08 Mole), benzene (8 ml).

5.1.2 Reaction of Butadiene with Phenol

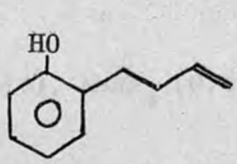
Butadiene was found to react similarly to isoprene; the $RhCl(PPh_3)_3$ - NaOPh system gave a 20% conversion of phenol to the six phenols LVI - LXI in the proportions shown (Expt. Rh/15). They were separated by distillation and preparative glc, and characterised spectroscopically. As in the case of the isoprene reactions, small amounts of


LVI (2%)


LIX 35%


LVII (23%)


LX < 1%

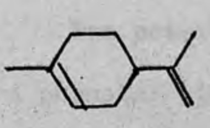

LVIII (34%)

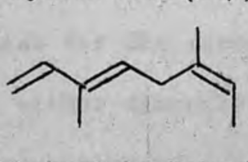

LXI 6%

lower-boiling products were obtained, but were not isolated. Reaction conditions were: $RhCl(PPh_3)_3$ (0.5 mMole), sodium phenoxide (0.5 mMole), phenol (0.2 Mole), isoprene (0.1 Mole), benzene (35 ml), 85°/24h.

5.1.3 Reaction of Isoprene with Methanol

When isoprene and methanol were treated with the catalyst system $RhCl_3\ 3H_2O$ - NaOPh, volatile compounds (probably methyl isoprene-monomer ethers) were the main products, which were not investigated. However, small amounts of dimers were obtained (about 5% conversion of isoprene). These were separated by preparative gas liquid chromatography to give two dimers, the linear LI (70%) and the cyclic XLV (30%). No other dimers or


XLV


LI

methyl-isoprene dimer ethers were obtained in detectable amounts. The dimer XLV and an authentic sample of limonene had identical glc retention times and nmr spectra. Reaction conditions were: $RhCl_3\ 3H_2O$ (0.5 mMole), NaOPh (2.5 mMole), isoprene (0.5 Mole), methanol (0.5 Mole), 85°/24h (Expt. Rh/10).

When a $RhCl(PPh_3)_3 - NaBH_4$ catalyst system was used with isoprene and methanol, no organic products were observed. However, a yellow crystalline complex was isolated from the reaction mixture and characterised by its infrared spectrum, melting-point and elemental analysis as trans-$Rh(CO)Cl(PPh_3)_2$.

Reaction conditions were : $RhCl(PPh_3)_3$ (0.5 mMole), $NaBH_4$ (0.5 mMole), isoprene (0.5 Mole), methanol (0.5 Mole), 85°/24h).

5.2 DISCUSSION

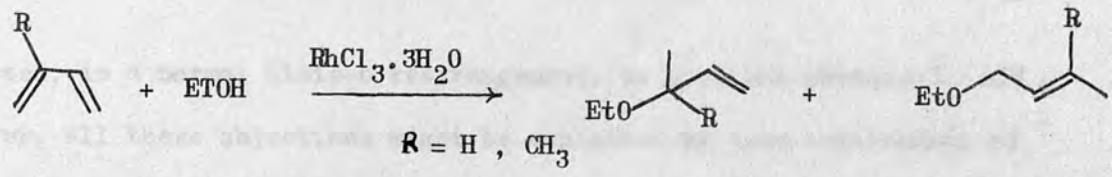
Two examples of the telomerisation of butadiene with phenol by rhodium-complex catalysts have been reported :

$$+ \ PhOH \xrightarrow[NaOPh,\ 80\text{-}100^{\circ}]{RhCl(PPh_3)_3} PhO\ CH_2CH{=}CH\ CH_2CH_2CH_2CH = CH_2 \qquad \text{(Ref. 39)}$$

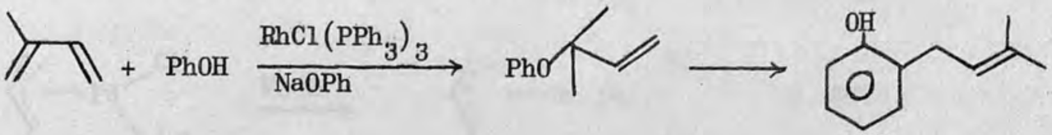
$$+ \ PhOH \xrightarrow[NaOPh]{Rh(OPh)(PPh_3)_3} PhO\ CH_2CH{=}\ CH\ CH_2CH_2CH_2CH = CH_2 \qquad \text{(Ref.43)}$$

The first of these reports is in direct conflict with our findings that alkenylated phenols are the major products, and that no phenyl isoprene-dimer ethers are obtained using the $RhCl(PPh_3)_3 - NaOPh$ catalyst system. Both components of this system are essential for the reaction to proceed. The role of the sodium phenoxide may be the same as it appears to be in the case of palladium catalysis, i.e. to remove the chloro ligand from the coordination sphere of the metal atom.

Two possibilities seem to exist for the formation of these substituted phenols: that they are formed either directly, or via phenyl butenyl ethers, with some kind of Claisen rearrangement. 1.3-Dienes and alcohols react in the presence of a rhodium chloride catalyst to give alkyl butenyl ethers(152,153), e.g.

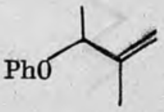


It seems possible that phenol and butadiene or isoprene might react similarly in the presence of the $RhCl(PPh_3)_3$ - NaOPh catalyst to yield initially phenyl butenyl ethers, which could then, in a Claisen-type rearrangement, give the substituted phenols as the final products :

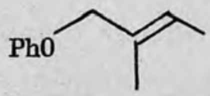


LII

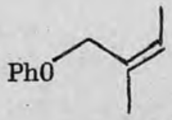
Some support is provided for this by the fact that small amounts of low-boiling products were also formed in the reaction. These were not separated, but they had the same glc retention times as the phenyl isoprene-monomer ethers XLVI - XLIX obtained from the reaction of isoprene and phenol in the presence of the zero-valent nickel complexes (see Chapter IV).



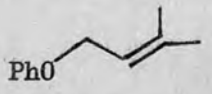
XLVI



XLVII



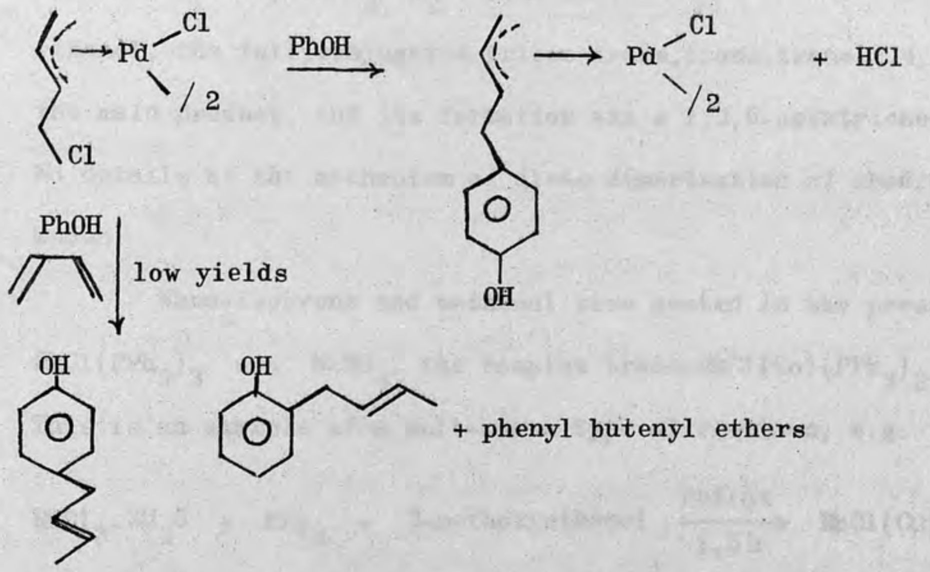
XLVIII



XLIX

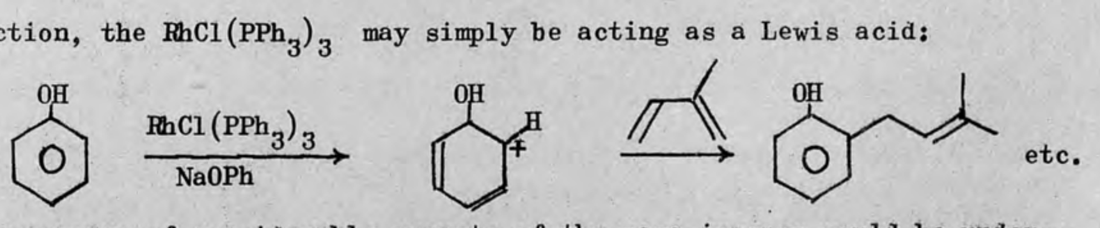
Several objections could be raised to this invocation of Claisen rearrangement. Firstly, much higher temperatures that the 85° employed here are generally required - often in the range of $200 - 220^\circ$. Secondly, the Claisen rearrangement usually gives almost exclusively the ortho-substituted phenol, whereas in our reaction appreciable amounts of the para-isomer have also formed. Thirdly, the ortho-allyl phenol LII is in fact only a minor product; the major products L and LIII have a terminal double bond in the side-chain. Double-bond isomerisation is a possibility, but the 2-alkenyl product is probably thermodynamically more stable, so any isomerisation would be expected to favour LII over LI and LIV over LIII. Fourthly, none of the ethers XLVI - XLIX identified by glc would be expected, in a normal Claisen rearrangement, to give the phenols L / LIV. However, all these objections might be explained by some involvement of the rhodium complex in the transformations.

The other possibility is that the substituted phenols are formed directly. C-Alkenylation of phenols by a palladium complex has already been reported, although no details of the mechanism are known(39):



In this case, it may be noted, a 2-alkenyl side-chain was obtained.

A 2-alkenyl side-chain is also obtained via the Friedel-Crafts reaction, when isoprene and phenol are treated with 71% orthophosphoric acid(54) to give the phenols LIL and LIV. In the rhodium-catalysed reaction, the $RhCl(PPh_3)_3$ may simply be acting as a Lewis acid:

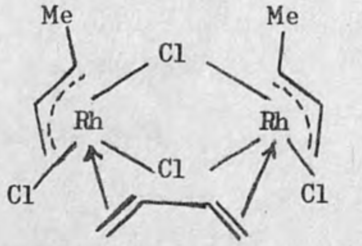


The presence of considerable amounts of the para-isomers would be understandable if a Friedel-Crafts reaction were involved; however, it is surprising that anisole does not also react.

In conclusion, no evidence is at present available for distinguishing between the two possible routes of formation of the substituted phenols (via phenyl ethers or directly).

The dimerisation of isoprene with a $RhCl_3.3H_2O$ - NaOPh catalyst in methanol solution was found to yield one linear head-to-head dimer LI in small conversions but selectively.

An isoprene analogue of the butadiene complex LXIV has not been isolated$^{(155)}$, but may be implicated. When butadiene was dimerised by $RhCl_3$ $3H_2O$ - KOAc in ethanol, the fullyconjugated triene trans,trans,trans-2,4,6-octatriene was the main product, and its formation via a 1,3,6-octatriene was suggested$^{(42)}$. No details of the mechanism of diene dimerisation of rhodium complexes are known.



LXIV

When isoprene and methanol were heated in the presence of $RhCl(PPh_3)_3$ and $NaBH_4$, the complex trans-$RhCl(Co)(PPh_3)_2$ was obtained. This is an example of a well-known type of reaction, e.g.

$$RhCl_3.3H_2O + PPh_3 + \text{2-methoxyethanol} \xrightarrow[1,5\,h]{reflux} RhCl(CO)(\rho Ph_3)_2 \qquad (Ref.156)$$

$$RhCl_3(PEt_3)_3 + KOH + EtOH \xrightarrow[1,5\,h]{reflux} RhCl(CO)(PEt_3)_2 \qquad (Ref.157)$$

CHAPTER VI

Section A of this chapter describes experimental procedure for Chapters III, IV and V. Section B gives spectral details and structure of the products.

SECTION A

EXPERIMENTAL DETAILS

Purification of Reagents

Isoprene was dried by refluxing over calcium hydride and distilled under nitrogen (bp 34-35°). It was stored in a refrigerator.

Analar phenol was distilled under reduced pressure.

Methanol was dried by the 'magnesium-iodine' method and distilled under nitrogen. It was stored over molecular sieves, type 3A.

Benzene was dried with sodium wire, distilled under N_2 and stored over molecular sieves type 4A.

6.1 GENERAL EXPERIMENTAL PROCEDURE

Reactions were carried out in ampoules of approximately 100 cm^3 capacity, made of Pyrex tubing (26 mm o.d., 22 mm i.d.). They were connected to a standard vacuum line by a B24 socket. In the general procedure, the solid reactants were placed in the ampoule (working under nitrogen if necessary); the ampoule was then attached to the vacuum line, frozen down with liquid nitrogen and pumped down to about 10^{-3} mm Hg. Meanwhile, elsewhere on the line, the liquid reactants were degassed by three cycles of the 'freeze-pump-thaw' method. They were then condensed into the ampoule which was sealed at the constriction and annealed. After warming to room temperature the ampoule was briefly shaken to ensure dissolution of the catalyst; it was then placed in a thermostatted oil-bath for the required period.

After the ampoule had been opened, its contents were quickly transferred to a stoppered flask, and examined by analytical glc prior to work-up. Analytical glc was performed on a Pye Unicam Series 104 chromatograph, using a 5 ft column packed with 10% polyethylene glycol 20 M on Celite; peak areas were electronically integrated with a Hewlett-Packard 3370 integrator. A Gow-Mac gas density meter was originally used to determine product ratios, but some trouble was experienced in obtaining a steady base-line, and a flame ionization detector was employed instead for the rest of the measurements. Comparison of results obtained on the same sample showed that the difference in product ratios was negligible.

Preparative glc was done on a Pye Unicam Series 105 Chromatograph. Two columns were used; a 30 ft × $\frac{3}{8}''$ o.d. column packed with 15% PEG 20 M on Celite (Column A), and a 15 ft × $\frac{3}{8}''$ o.d. column packed with 20% silicone oil on Celite (Column B). Column A was also employed to determine retention data for most of the isoprene dimers. The Kováts Retention Index scheme$^{(159)}$ was used; this depends on the n-alkanes, each of which is, by definition, allotted a retention index one hundred times its carbon number. The retention index I_x of a compound x is then

$$I_x = \frac{100}{b}\,(\log t'_{RX} - a)$$

where t'_{RX} is the adjusted retention time of x, and a and b are constants for the instrument and operating conditions.

Thus considering an alkane $n\text{-}C_NH_{2N+2}$, whose Kováts index I_N is by definition 100 N, we may write

$$I_N = 100\,N = \frac{100}{b}(\log t'_{RN} - a)$$

or

$$\log t'_{RN} = a + bN\ .$$

The constants a and b were determined for the conditions used (Column A; 100°, 80 cm^3/min. for $C_{10}H_{16}$ hydrocarbon, and 150°, 80 cm^3/min. for methyl and ethyl isoprene-dimer ethers) by injecting a mixture of n-alkanes ($C_5 - C_{12}$) and measuring their retention times t_{RN}. Using the equations

$$t'_{RN} = t_{RN} - t_{R_{air}}$$

and

$$t_{R_{air}} = \frac{t^2_{R(N+1)} - t_{RN}\, t_{R(N+2)}}{2t_{R(N+1)} - t_{RN} - t_{R(N+2)}}$$

the adjusted retention times t'_{RN} of the n-alkanes were calculated. A plot of log t'_{RN} against N gave a straight line, whose slope was b and whose y-intercept was a. At 100° and 80 ml/min, a = - 1,395 and b = 0,275. At 150° and 80 ml/min a = - 0.957 and b = 0,186. The Kováts Indices of any sample could then be calculated from its retention time and the values of $t_{R_{air}}$, a and b at the condition used. The Kováts Indices of those compounds determined are given on the appropriate pages of Section B.

6.2 EXPERIMENTAL DETAILS FOR CHAPTER III

6.2.1 Preparation of Palladium Complexes

$Pd(PPh_3)_4$

This air-sensitive complex was prepared from palladium chloride by the method of Coulson(160). Yield was 90%. The pale yellow crystals were stored under nitrogen in a sealed tube, but could be manipulated in air.

$PdCl_2(PPh_3)_2$

$PdCl_2$ (0.02 Mole, 3.55 g) was dissolved in concentrated hydrochloric acid and the solution was evaporated to dryness. The residue was redissolved in hydrochloric acid and again evaporated to dryness. It was then dissolved in a 1:1 mixture of ethanol and hydrochloric acid, and added to a solution of triphenylphosphine (0.1 Mole, 26.2g) in ethanol. The lemon-yellow solid was filtered off, washed with ethanol (50 cm^3) and ether (50 cm^3) and dried under vacuum. After recrystallisation from chloroform, washing with ether and drying under vacuum, the final yield was 9.9 g (73%).

$PdCl_2(P\ Bu_3)_2$

Sodium tetrachloropalladite (0.0136 Mole, 4 g) was suspended in ethanol (50 ml) under a nitrogen atmosphere and tributylphosphine (0.028 Mole, 7 cm^3) was added. After stirring for two hours the mixture was filtered. After removal of ethanol on a rotary evaporator, the product was obtained as yellow plates; yield was 7.31 g (92%). Recrystallisation from chloroform gave crystals of m.p. 65° (lit[161] 66°).

$(\pi\text{-}C_3H_5)_2Pd_2Cl_2$

$PdCl_2$ (0.034 Mole, 6 g) was boiled with 50% acetic acid and filtered. Freshly distilled allyl chloride (0.052 Mole, 5 g) was added to the filtrate. After stirring for 1 hour, the product was extracted with benzene, evaporated to dryness and recrystallised from benzene to m.p. 160° (lit[162] 160°). The yield was 3.4 g (55%).

$Pd(PhCN)_2Cl_2$

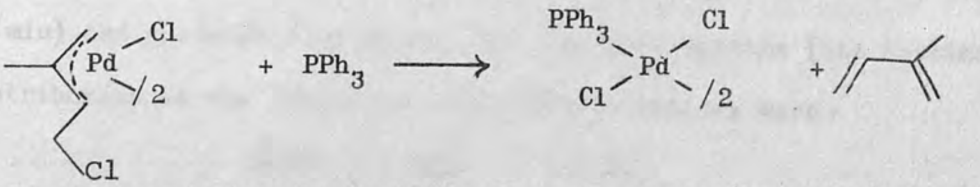
This complex was prepared by the method of Kharasch(163). Yield 73%.

Di-μ-chloro-di(4-chloro-2-methyl-but-2-enyl) dipalladium

This previously unreported complex was prepared by a method analogous to that for the butadiene complex(164); isoprene (10 cm^3) was added to $Pd(PhCN)_2Cl_2$ (0.01 Mole, 4 g) dissolved in the minimum benzene. The deep red colour changed to yellow almost immediately. Addition of petroleum ether (bp 40-60°) precipitated the product, which was filtered off and recrystallised from benzene. M.p. 118-120° (d). Yield 1.72 g (70%). A micro-analysis gave the results :

		C	H	Cl
	Calculated :	24.47	3.29	28.88
	Found :	24.58	3.42	28.78 .

$Pd_2Cl_4(PPh_3)_2$



Treatment of di-μ-chloro-di(4-chloro-2-methyl-but-2-enyl) dipalladium (0.002 Mole, 1 g) with the stoicheimetric amount of triphenylphosphine (0.004 Mole, 1.05 g) in benzene solution gave the product as deep orange crystals. Isoprene was detected by glc in the filtrate. The infrared spectrum of the product showed the presence of both bridging and terminal Pd-Cl bonds, at 260 cm^{-1} and 358 cm^{-1} respectively(165).

		C	H	Cl
Microanalysis :	Calculated :	49.13	3.43	16.13
	Found :	49.31	3.61	16.35

$Pd(acac)_2$

Palladium chloride (0.023 Mole, 4 g), sodium acetate (10 g) and acetylacetone (25 ml) were stirred overnight at room temperature in 50% aqueous methanol solution (100 cm^3). The yellow precipitate obtained was filtered, washed with water and methanol, and recrystallised from benzene. Yield 5.3 g (77%).

6.2.2 Palladium-Catalysed Reactions
Isoprene-Methanol Telomerisations

Expt. Pd/7

$PdCl_2(PPh_3)_2$ (0.5 mMole, 0.3509 g), sodium borohydride (0.5 mMole, 0.0189 g), isoprene (0.5 Mole, 50 cm^3) and methanol (0.5 Mole, 20.4 cm^3) were heated at 85° for 24 hours. The product was distilled into a liquid nitrogen trap under reduced pressure and then fractionally distilled to give (i) bp 35-70°/760 mm, isoprene and methanol, 21 g,

(ii) bp 45-75°/5.25 mm, dimers and telomers 25.4 g. (iii) pot residue, higher oligomers, 2.5 g. Glc analysis of the dimer and telomer fraction showed that its composition was 19% dimers and 81% telomers (i.e. methyl ethers). The ethers were separated by preparative glc (Column A, 130°, 60 cm^3/min) and characterised by nmr, ir and mass spectra (see Section B). The distribution of the ethers and their Kováts Indices were :

XXXIV	52%	1424
XXXV	9%	1398
XXXVI	22%	1367
XXXVII	2%	1338
XXXVIII	3%	1474
XXXIX	9%	1263
XI	3%	1310

From these results isoprene conversion was calculated to be 63%.

Expt. Pd/8

$PdCl_2(PBu_3)_2$ (0.5 mMole, 0.2907 g), sodium borohydride (0.5 mMole, 0.0189 g), isoprene (0.5 Mole, 50 cm^3) and methanol (0.5 Mole, 20.4 cm^3) were heated at 85° for 24 hours. Distillation into a cold trap, followed by fractional distillation, gave (i) bp 35-70° isoprene and methanol, 30 g, (ii) bp 35-65°/4 mm, dimers and telomers, 14.67 g. Fraction (ii) consisted of 33% trienes and 67% ethers. The ether distribution and the Kováts Indices were :

XXXIV	26%	1424
XXXV	5%	1398
XXXVI	52%	1368
XXXVII	10%	1336
XXXVIII	1%	1475
XXXIX	6%	1263
XL	1%	1308

Isoprene conversion was 38%.

Expt. Pd/10

$PdCl_2(PPh_3)_2$ (0.5 mMole, 0.3509 g), sodium borohydride (0.5 mMole, 0.0189 g), isoprene (0.5 Mole, 50 cm^3) and methanol (0.5 Mole, 20.4 cm^3) were kept at 25° for 24 hours. Distillation of the product gave: (i) bp 35-70°, isoprene and methanol, 40 g, (ii) bp 45-75°/5 mm, dimers and telomers, 3.1 g. The ethers were identified by comparison of retention times with authentic samples as:

XXXIV	17%	XXXVIII	1%
XXXV	1%	XXXIX	2%
XXXVI	70%	XL	1%
XXXVII	9%		

Ethers constituted 91% of fraction (ii), the remainder being dimers. Isoprene conversion was about 7.5%.

Expt. Pd/11

$PdCl_2(PBu_3)_2$ (0.5 mMole, 0.2907 g), sodium borohydride (0.5 mMole, 0.0189 g), isoprene (0.5 Mole, 50 cm^3) and methanol (0.5 Mole, 20.4 cm^3) were kept at 25° for 24 hours. Glc analysis revealed no products.

Expt. Pd/12

$Pd_2Cl_4(PPh_3)_2$ (0.5 mMole, 0.4396 g), sodium borohydride (0.5 mMole, 0.0189 g), isoprene (0.5 Mole, 50 cm^3) and methanol (0.5 Mole, 20.4 cm^3) were heated at 85° for 24 hours. Glc analysis revealed no products.

Expt. Pd/13

$PdCl_2(PPh_3)_2$ (0.5 mMole, 0.3509 g), triethylamine (0.5 mMole, 0.0505 g), isoprene (0.5 Mole, 50 cm^3) and methanol (0.5 Mole, 20.4 cm^3) were heated at 85° for 24 hours. No products were observed from glc analysis.

Expt. Pd/14

$PdCl_2(PPh_3)_2$ (0.5 mMole, 0.3509 g), sodium phenoxide (0.5 mMole, 0.0580 g), isoprene (0.5 Mole, 50 cm^3) and methanol (0.5 Mole, 20.4 cm^3) were heated at 85° for 24 hours. Distillation into a cold trap, followed by fractional distillation, gave (i) bp 35-70°/760 mm. isoprene and methanol, 16 g; (ii) bp 40-70°/3.75 mm, dimers and telomers, 29.0 g.

The composition of fraction (ii) was 27% dimers and 73% telomers. The distribution of telomers (identified by glc retention times) was:

XXXIV	61%	XXXVIII	3%
XXXV	3%	XXXIX	5%
XXXVI	25%	XL	2%
XXXVII	1%		

Isoprene conversion was 73%.

Expt. Pd/15

$Pd(PPh_3)_4$ (0.5 mMole, 0.5778 g), isoprene (0.5 Mole, 50 cm^3), and methanol (0.5 Mole, 20.4 cm^3) were heated for 24 hours at 85°. Fractional distillation of the product yielded (i) bp 35-70°, isoprene and methanol, 14 g; (ii) bp 40-70°/4 mm, dimers and telomers, 28.3 g; (iii) Pot residue, higher oligomers, 4.4 g. Fraction (ii) consisted of 12% trienes and 88% ethers. The ether distribution was:

XXXIV	60%	XXXVIII	3%
XXXV	1%	XXXIX	5%
XXXVI	26%	XL	4%
XXXVII	1%		

Isoprene conversion to dimers and telomers was 69%.

Expt. Pd/25

$PdCl_2(Pcy_3)_2$ (0.5 mMole, 0.3687 g), sodium phenoxide (0.5 mMole, 0.0580 g), isoprene (0.5 Mole, 50 cm^3), and methanol (0.5 Mole, 20.4 cm^3) were heated for 24 hours at 85°. Fractional distillation yielded (i) bp 35-70°, isoprene and methanol, 43 g; (ii) bp 40-70°/4 mm, dimers and telomers, 3.64 g. Fraction (ii) contained 84% ethers and 16% trienes. The distribution of ethers was:

XXXIV	12%	XXXVIII	1%
XXXV	2%	XXXIX	1%
XXXVI	67%	XL	1%
XXXVII	16%		

Isoprene conversion was 9%.

Expt. Pd/31

π-allylpalladium chloride dimer (0.25 mMole, 0.09148 g), sodium phenoxide (0.5 mMole, 0.0580 g), triphenylphosphine (0.5 mMole, 0.1311 g), isoprene (0.5 Mole, 50 cm^3) and methanol (0.5 Mole, 20.4 cm^3) were heated at 85° for 24 hours. Distillation of the product gave (i) bp 35-70°, isoprene and methanol, 13.5 g; (ii) bp 45-75°/5 mm, dimers and telomers, 31.3 g; (iii) pot residue, higher oligomers, 3.5 g. Fraction (ii) consisted of 33% trienes and 67% ethers. The distribution of ethers was:

XXXIV	56%	XXXVIII	2%
XXXV	6%	XXXIX	6%
XXXVI	27%	XL	2%
XXXVII	1%		

Isoprene conversion to dimers and telomers was 88%.

Expt. Pd/36

Pd(acac)$_2$ (0.5 mMole, 0.1522 g), triphenylphosphite (0.5 mMole, 0.1551 g), isoprene (0.5 Mole, 50 cm^3) and methanol (0.5 Mole, 20.4 cm^3) were heated at 85° for 24 hours. The product was distilled to give: (i) bp 35-70°, isoprene and methanol, 15 g; (ii) bp 45-75°/5 mm, dimers and telomers 31.3 g. Fraction (ii) consisted of 62% trienes and 38% ethers. The ether distribution was:

XXXIV	51%	XXXVIII	-
XXXXV	3%	XXXIX	-
XXXVI	40%	XL	1%
XXXVII	5%		

Isoprene conversion was 84%.

Expt. Pd/37

Pd(acac)$_2$ (0.5 mMole, 0.1522 g), triphenylphosphine (0.5 mMole, 0.1311 g), isoprene (0.5 Mole, 50 cm^3), and methanol (0.5 Mole, 20.4 cm^3) were heated at 85° for 24 hours. Distillation gave (i) bp 35-70°, isoprene and methanol, 15.2 g; (ii) bp 45-75°/5 mm, dimers and telomers, 31.5 g. Fraction (ii) consisted of 59% trienes and 41% ethers. The ether distribution was:

XXXIV	52%	XXXVIII	-
XXXV	4%	XXXIX	6%
XXXVI	34%	XL	-
XXXVII	4%		

Isoprene conversion was 84%.

6.2.3 Telomerisation of Isoprene with other Alcohols

Expt. Pd/16 - Ethanol

$Pd(PPh_3)_4$ (0.5 mMole, 0.5778 g), isoprene (0.5 Mole, 50 cm^3) and ethanol (0.5 Mole, 29.2 cm^3) were heated at 85° for 24 hours. The product was distilled to yield (i) bp 35°, isoprene, 13 g ; (ii) bp 77-80°, ethanol, 18.5 g ; (iii) bp 43-80°/4.25 mm, dimers and belomers, 17.8 g . Fraction (iii) consisted of 21% trienes and 79% ethyl ethers. The two major products were isolated by preparative glc (Column A, 165°, 60 ml/min.), and were identified as the triene XLI and the ether XLII; the latter constituted 80% of the ethers formed. Isoprene conversion was 44%.

Expt. Pd/22 - n-Propanol

$PdCl_2(PPh_3)_2$ (0.5 mMole, 0.3509 g), sodium phenoxide (0.5 mMole, 0.0580 g), isoprene (0.5 Mole, 50 cm^3) and n-propanol (0.5 Mole, 19.3 cm^3) were heated at 85° for 24 hours. Distillation of the product gave (i) bp 35°, isoprene 22 g , (ii) bp 96-98°, n-propanol, 28 g; (iii) bp 45-95°/4.25 mm, dimers and telomers, 9.5 g. Fraction (iii) contained 73% trienes and 27% n-propyl ethers. The major triene was identified as XLI by comparison of retention time with an authentic sample. XLI constituted > 85% of the trienes formed. The major n-propyl ether was not isolated but was assumed to be the n-propyl analogue of XLII.

Expt. Pd/24 - iso-Propanol

$PdCl_2(PPh_3)_2$ (0.5 mMole, 0.3509 g), sodium phenoxide (0.5 mMole, 0.0580 g), isoprene (0.5 Mole, 50 cm^3) and iso-propanol (0.5 Mole, 19.1 cm^3) were heated at 85° for 24 hours. Analysis of the product by glc showed that small amounts of cyclic dimers were the only products.

Expt. Pd/23 - t-Butanol

$PdCl_2(PPh_3)_2$ (0.25 mMole, 0.1755 g), sodium phenoxide (0.25 mMole, 0.0079 g), isoprene (0.25 Mole, 25 cm^3) and t-butanol (0.25 Mole, 23.6 cm^3) were heated for 24 hours at 85°. No products were obtained other than thermally-formed dimers.

6.2.4 Isoprene-Phenol Telomerisations

Expt. Pd/26

$PdCl_2(PPh_3)_2$ (0.1 mMole, 0.0702 g), sodium phenoxide (0.1 mMole, 0.0116 g), isoprene (0.3 Mole, 30 cm^3), phenol (0.1 Mole, 9.4 g) and benzene (20 cm^3) were kept at 25° for 24 hours. Glc analysis showed traces of the phenyl ether XXIV as the only product.

Expt. Pd/27

$PdCl_2(PPh_3)_2$ (0.1 Mole, 0.0702 g), sodium phenoxide (0.1 mMole, 0.0116 g), isoprene (0.3 Mole, 30 cm^3), phenol (0.1 Mole, 9.4 g) and benzene (20 cm^3) were heated at 85° for 24 hours. The conversion of phenol was estimated by analytical glc, using standard solutions of phenol in benzene, as approximately 40%. Analytical glc also gave the product distribution as 27% trienes and 73% phenyl ethers. The distribution of the ethers was found to be:

XXIV	63%	XXVII	1%
XXV	12%	XXVIII	3%
XXVI	21%		

In order to separate these ethers, both for their quantisation, and for their characterisation, Column B was used (185°, 120 cm/min.), as the two ethers XXV and XXVI were inseparable on Column A.

Expt. Pd/28

$(\pi\text{-}C_3H_5)_2Pd_2Cl_2$ (0.05 mMole, 0.0183 g), sodium phenoxide (0.1 mMole, 0.0116 g), isoprene (0.3 Mole, 30 cm^3), phenol (0.1 Mole, 9.4 g) and benzene (20 cm^3) were kept at 0° for 24 hours. Some decomposition to metallic palladium occurred. Glc analysis revealed no product other than traces of XXIV.

Expt. Pd/29

$(\pi\text{-}C_3H_5)_2 Pd_2Cl_2$ (0.05 mMole, 0.0183 g), sodium phenoxide (0.1 mMole, 0.0116 g), isoprene (0.3 Mole, 30 cm^3), phenol (0.1 Mole, 9.4 g) and benzene (20 cm^3) were kept at 25° for 24 hours. No products other than traces of XXIV were found by analytical glc, and considerable decomposition to palladium metal occurred.

Expt. Pd/32

$(\pi\text{-}C_3H_5)_2 Pd_2Cl_2$ (0.05 mMole, 0.0183 g), sodium phenoxide (0.1 mMole, 0.0116 g), triphenylphosphine (0.1 mMole, 0.0262 g), isoprene (0.3 Mole, 30 cm^3), phenol (0.1 Mole, 9.4 g) and benzene (20 cm^3) were heated at 85° for 24 hours. Phenol conversion was estimated as 86%, and the product was composed of 18% trienes and 82% phenyl ethers. The distribution of the phenyl ethers was:

XXIV	33%	XXVII	4.5%
XXV	6%	XXVIII	7.5%
XXVI	49%		

Expt. Pd/34

$(\pi\text{-}C_3H_5)_2Pd_2Cl_2$ (0.05 mMole, 0.0183 g), sodium phenoxide (0.1 mMole, 0.0116 g), tributylphosphine (0.1 mMole, 0.0202 g), isoprene (0.3 Mole, 30 cm^3), phenol (0.1 Mole, 9.4 g) and benzene (20 cm^3) were heated at 85° for 24 hours. Phenol conversion was estimated at 69%, the dimeric fraction being composed of 6% trienes and 94% phenyl ethers. The ether distribution was:

XXIV	74.5%	XXVII	0.5%
XXV	15%	XXVIII	3%
XXVI	7%.		

Expt. Pd/41

$PdCl_2(PBu_3)_2$ (0.1 mMole, 0.0581 g), sodium phenoxide (0.1 mMole, 0.0116 g), isoprene (0.3 Mole, 30 cm^3), phenol (0.1 Mole, 9.4 g) and benzene (20 cm^3) were heated at 85° for 24 hours. No products were observed other than traces of XXIV.

Expt. Pd/43

$PdCl_2(Pcy_3)_2$ (0.1 mMole, 0.0737 g), sodium phenoxide (0.1 mMole, 0.0116 g), isoprene (0.3 Mole, 30 cm^3), phenol (0.1 Mole, 9.4 g) and benzene (20 cm^3) were heated at 85° for 24 hours. Phenol conversion was 20%; the product was exclusively phenyl isoprene-dimer ethers in the proportions shown :

XXIV	87%	XXVII	-
XXV	-	XXVIII	-
XXVI	13%		

Expt. Pd/44

$Pd_2Cl_4(PPh_3)_2$ (0.05 mMole, 0.0440 g), sodium phenoxide (0.1 mMole, 0.0116 g), isoprene (0.3 Mole, 30 cm^3) phenol (0.1 Mole, 9.4 g) and benzene (20 cm^3) were heated at 85° for 24 hours. No products were obtained.

6.2.5 Isoprene-Water Telomerisation

Expt. Pd/38

For this reaction a 400 ml autoclave, fitted with Teflon liner and stirrer, was used. $Pd(acac)_2$ (1 mMole, 0.3046 g), triphenylphosphine (3 mMole, 0.7869 g), isoprene (2 Mole, 200 cm^3), water (2 Mole, 36 cm^3) and acetone (100 cm^3) were placed in the autoclave. After tightening down the autoclave head, carbon dioxide was admitted to a pressure of approximately 50 psi, and the autoclave was heated at 95° for 18 hours. Glc analysis of the product showed the presence of small amounts of product. Fractional distillation yielded 8 g of dimeric fraction (bp 35-95°/3 mm), consisting of 92% trienes and 8% alcohols. The three alcohol peaks were separated by preparative glc ; (Column A, 160°, 120 ml/min.); the major product (63%) was not identified, since its nmr spectrum could not be interpreted; the two minor products were identified as tail-to-tail dimers, LXVIII (28%) and LXIX 9%. All three compounds had a parent ion m+/e 154 in the mass spectrum, corresponding to $C_{10}H_{18}O$.

6.2.6 Other Palladium-Catalysed Reactions

Expt. Pd/18a

$PdCl_2(PPh_3)_2$ (0.5 mMole, 0.3509 g), sodium phenoxide (0.5 mMole, 0.0580 g), methanol (15 cm^3) and a mixture of methyl isoprene-dimer ether obtained from Expt. Pd/10 (6 cm^3) were heated at 85° for 24 hours. The ratios of the various ethers were then re-measured by analytical glc . The results were (original values in parenthesis) :

XXXIV	17%	(17%)	XXXVIII	1%	(1%)
XXXV	0%	(<1%)	XXXIX	2%	(2%)
XXXVI	70%	(70%)	XL	1%	(<1%)
XXXVII	9%	(9%)			

Expt. Pd/18b

$PdCl_2(PPh_3)_2$ (0.5 mMole, 0.3509 g), sodium phenoxide (0.5 mMole, 0.0580 g), methanol (15 cm^3) and a mixture of methyl isoprene-dimer ether from Expt. Pd/15 were heated at 85° for 24 hours. The ratio of the various ethers were then re-measured by glc . The results were (original values in parenthesis) :

XXXIV	60%	(60%)	XXXVIII	3%	(2%)
XXXV	2%	(1%)	XXXIX	5%	(4%)
XXXVI	25%	(27%)	XL	3%	(3%)
XXXVII	2%	(3%)			

Expt. Pd/18c

This experiment was performed exactly as in Expt. Pd/18b, except that benzene (15 cm^3) was used as solvent. Results were :

XXXIV	61%	(60%)	XXXVIII	2%	(2%)
XXXV	2%	(1%)	XXXIX	4%	(4%)
XXXVI	27%	(27%)	XL	3%	(3%)
XXXVII	1%	(3%)			

Expt. Pd/19

$(\pi\text{-}C_3H_5)_2Pd_2Cl_2$ (0.05 mMole, 0.0183 g), sodium phenoxide (0.1 mMole, 0,0116 g) and a mixture of phenyl isoprene-dimer ethers (0.1 Mole, 2.3 g) were heated to 100° at 0.1 mm Hg. Phen~~y~~ol and trienes distilled into a cold trap as they were formed. The yield was ≃94%. The trienes were separated by preparative glc (column A, 90°, 100 cm^3/min) and characterised as XXIX - XXXIII. The constitution of the original ether mixture was :

XXIV	~~6~~75%
XXV	5%
XXVI	9%
XXVII	9%

The constitution of the product was :

XXIX	70%
XXX	3%
XXXI	9%
XXXII	8%
XXXIII	8% .

6.3 EXPERIMENTAL DETAILS FOR CHAPTER IV

6.3.1 Preparation of Nickel Complexes

$NiCl_2(Pcy_3)_2$

A suspension of anhydrous nickel chloride (0.025 Mole, 2.94 g) in ethanol (250 cm^3) was treated with tricyclohexylphosphine (0.075 Mole, 21 g). After refluxing for four hours the red-purple precipitate was filtered off, washed with water (2 × 50 cm^3), ethanol (2 × 25 cm^3) and ether (25 cm^3), and dried under vacuum. Yield was 14.83 g (86%).

$Ni(H)Cl(Pcy_3)_2$

This complex was prepared by the literature method(166). Yield was (43%). The infrared spectrum of the product (Nujol mull) had a band at 1918 cm^{-1} (lit. 1916 cm^{-1}) assignable to the Ni-H stretch.

$Ni(H)(BH_4)(Pcy_3)_2$

This complex was prepared by the literature method(167). The yield was 90%. The complex had m.p. 120-125° (d) (lit[167] 121-125° (d)); the infrared spectrum (nujol mull) had a band at 1920 cm^{-1}, assignable to the Ni-H stretch.

$Ni(CH_2=CH CN)_2$

The complex was prepared by the literature method(168), from nickel tetracarbonyl and acrylonitrile. The yield was 84%. The compound was pyrophoric in air, and was prepared, stored and used under nitrogen.

$Ni[P(OPh)_3]_4$

The complex was prepared from $Ni(NO_3)_2.6H_2O$ and triphenylphosphite by the literature method(169). The yield of crude product was 88%; it was recrystallised by dissolution in the minimum volume of benzene followed by drop-wise addition of methanol. It was stable for long periods when stored in a stoppered flask; on exposure to air it slowly turned pale green.

$Ni[P(OEt)_3]_4$

This complex was prepared from $NiCl_2.6H_2O$ and triethyl phosphite by a literature method(170). Yield was 40%. The white crystals were slowly oxidised in air, but were apparently stable for long periods in a stoppered flask.

$Ni(acac)_2$

The literature method was used(171). The crude product was purified by vacuum sublimation at 190°.

6.3.2 Preparation of phenyldi(isopropoxy)phosphine

Phenyldi(isopropoxy)phosphine was prepared from isopropanol and dichlorophenylphosphine by the literature method(172). The yield was 79%.

6.3.3 Nickel-Catalysed Reactions
Isoprene-Methanol Telomerisations

Expt. Ni/21

$Ni(H)(BH_4)(Pcy_3)_2$ (0.5 mMole, 0.3176 g), isoprene (0.5 Mole, 50 cm^3) and methanol (0.5 Mole, 20.4 cm^3) were heated at 85° for 24 hours. Fractional distillation of the product yielded (i) bp 35°, isoprene, 28 g; (ii) bp 67-68° methanol, 15.5 g; (iii) bp 40-50°/5 mm, dimers, 2.2 g. The dimers consisted solely of trienes; no methyl ethers were obtained. The trienes were separated by preparative glc (Column A, 105° C, 80 cm^3/min.) and identified by nmr and infrared spectra. The proportions of the trienes were found by glc to be:

XXIX	13%	XXXII	18%
XXX	27%	XLI	9%
XXXI	17%	XLV	16%

Expt. Ni/22

$Ni(H)Cl(Pcy_3)_2$ (0.5 mMole, 0.3280 g), isoprene (0.5 Mole, 50 cm^3) amd methanol (0.5 Mole, 20.4 cm^3) were heated at 85° for 24 hours. Glc analysis revealed no products other than a small amount of the thermally-formed cyclodimer XLV.

Expt. Ni/27

$Ni(CH_2CH{=}CN)_2$ (0.592 mMole, 0.0976 g), tributylphosphine (0.592 mMole, 0.1198 g), isoprene (0.5 Mole, 50 cm^3) and methanol (0.5 Mole, 20.4 cm^3) were heated at 85° for 24 hours. Distillation yielded three fractions: (i) bp 35° isoprene, 24 g; (ii) bp 68° methanol 15 g; (iii) bp 40-50°/5 mm, dimers, 6.0 g. The dimers were characterised by comparison of their Kováts Indices with the products of Expt. Ni/28. The product distribution was (by analytical glc, using the electronic integrator) :

		Kováts Index			Kováts Index
XXX	29%	1149	XLIII	6%	1183
XXXI	23%	1131	XLV	16%	1202
XXXII	9%	1126	Unidentified	6%	
XLI	11%	1187			

Isoprene conversion was 18%.

Exp. Ni/28

$Ni/CH_2CH = CN)_2$ (0.74 mMole, 0.1224 g), triphenyl phosphine (0.74 mMole, 0.1943 g), isoprene (0.5 Mole, 50 cm^3) and methanol (0.5 Mole 20.4 cm^3) were heated at 85° for 24 hours. Fractional distillation yielded (i) bp 35°, isoprene, 26 g; (ii) bp 67-68° methanol, 15.1 g; (iii) bp 40-50°/4 mm, dimers, 5.0 g. The dimers were separated by preparative glc (Column A, 90°, 80 ml/min) and characterised by nmr, and infrared spectra. Their proportions and Kováts Indices were ;

		Kováts Index			Kováts Index
III	12%	1148	XLIII	11%	1183
XXXI	19%	1130	XLIV	14%	1211
XXXII	11%	1125	XLV	12%	1202
XLI	14%	1187	unidentified	7%	

Isoprene conversion was 15%.

Expt. Ni/29

$Ni(CH_2CH=CN)_2$ (0.825 mMole, 0.1360 g), $P(OEt)_3$ (0.825 mMole, 0.1371 g), isoprene (0.5 Mole, 50 cm^3) and methanol (0.5 Mole, 20.4 cm^3) were heated at 85° for 24 hours. Distillation of the product gave (i) bp 35°, isoprene 30 g; (ii) bp 68°, methanol 15.5 g; (iii) bp 40-51°/5 mm, dimers 1.2 g. The dimers were identified by their Kováts Indices as:

		Kováts Index			Kováts Index
XXIX	2%	1099	XLI	21%	1187
XXX	2%	1148	XLIII	$20\frac{1}{2}$	1183
XXXI	2%	1129	XLIv	14%	1210
XXXII	1%	1124	XLV	28%	1202
			unidentified	10%	

Isoprene conversion was only 3.4%.

Expt. Ni/31

Anhydrous nickel chloride (0.5 mMole, 0.0646 g), phenyldisopropoxyphosphine (0.75 mMole, 0.1700 g), sodium borohydride (0.1 mMole, 0.0043 g) isoprene (0.5 Mole, 50 cm^3) and methanol (0.5 Mole, 20.4 cm^3) were heated at 85° for 25 hours. Glc analysis showed no products other than small amounts of thermal dimers.

Expt. Ni/32

$Ni(acac)_2$ (1.0 mMole, 0.2621 g), $PhP(O^iPr)_2$ (1.5 mMole, 0.3388 g), sodium borohydride (0.016 g), isoprene (0.2 Mole, 20 cm^3) and methanol (1.0 Mole, 40.8 cm^3) were heated at 85° for 24 hours. The main products were methyl isoprene-monomer others, but very small amounts of trienes and methyl isoprene-dimer ethers were also obtained. The proportions of the dimers obtained were:

		Kováts Index
XXIX	33%	1099
XXX	11%	1148
XLI	3%	1188
XLV	53%	1201

The Kováts Indices of the three methyl ethers formed were 1302, 1338 and 1364. Their mass spectra all had a parent ion at m+/e 168 as required for $C_{11}H_{20}O$, but were different from the mass spectra of the methyl ethers obtained by palladium catalysed telomerisation. Because of the small amounts available, they were not investigated further.

6.3.4 Isoprene-Phenol Telomerisation

Expt. Ni/34

$Ni[P(OEt)_3]_4$ (1.0 mMole, 0.7233 g), isoprene (0.5 Mole, 5.0 cm^3), and phenol (0.1 Mole, 9.4 g) were heated at 85° for 24 hours. The phenol conversion was estimated at 10% by the use of standard phenol solutions and analytical glc. The product peaks were assigned by comparison of their retention times with those of the products of Expt. Ni/35. The proportions of the products were measured by analytical glc with the electronic integrator; they were :

XLVI	56%	XLIX	9%
XLVII	3%	L	17%
XLVIII	7%		

Expt. Ni/35

$Ni[P(OPh)_3]_4$ (1.0 mMole, 1.3000 g), isoprene (0.5 Mole, 50 cm^3) and phenol (0.1 Mole, 9.4 g) were heated at 85° for 24 hours. Glc analysis of the product showed several peaks, and a phenol conversion of 45%. The product was then washed with 4N NaOH (3 × 20 cm^3) to remove phenol, washed with distilled water (3 × 15 cm^3) and dried over anhydrous magnesium sulphate. Distillation yielded (i) bp 35° isoprene; (ii) bp 63-79°/7.5 mm, phenyl isoprene-monomer-ethers, 6.7 g ; (iii) bp 96-100°/0.1 mm, phenyl isoprene dimer 0.9 g. Fractions (ii) and (iii) were separated by preparative glc. (Column A, 170° for fraction (ii), 210° for fraction (iii), 140 cm^3/min.), and identified by nmr and ir spectra. Glc analysis of the complete reaction mixture gave the following result :

XLVI	64%	XXVI	2%
XLVII	4%	XXIV	5%
XLVIII	6%	L	5%
XLIX	14%.		

6.4 EXPERIMENTAL DETAILS FOR CHAPTER V

6.4.1 Preparation of Rhodium Complexes

$Rh(Cl(PPh_3)_3$

Rhodium chloride ($RhCl_3.nH_2O$) (10 mMole, 2.63 g) was refluxed with excess triphenylphosphine (60 mMole, 15.74 g) in ethanol (250 cm^3) for three hours. The red-purple crystals were filtered off and washed with ethanol (3×25 cm^3) and ether (2×25 cm^3). They were dried in vacuo. Yield was 8.41 g (92%).

$RhCl_2(Pcy_3)_2$

This complex was prepared by the literature method(173). The yield was 2.85 g (78%).

$Rh(nbd)_2(BF_4)$

A sample of this complex was supplied by Dr P. Powell.

6.4.2 Isoprene-Methanol Reactions

Expt. Rh/2

$RhCl(PPh_3)_3$ (0.5 mMole, 0.4625 g), sodium borohydride (0.5 mMole, 0.019 g), isoprene (0.5 Mole, 50 cm^3) and methanol (0.5 Mole, 20.4 cm^3) were heated at 85° for 24 hours. On cooling, the reaction mixture deposited yellow crystals whose melting point (209° (d))(174), infrared spectrum(174) (strong band at 1960 cm^{-1}) and microanalysis confirmed that t the complex $Rh(CO)Cl(PPh_3)_2$ had been formed.

	C	H	Cl
Calculated for $C_{37}H_{30}OClP_2Rh$:	64.26	4.37	5.13
Found :	64.02	4.51	5.07

Glc analysis of the reaction mixture did not indicate the formation of any isoprene oligomers.

Expt. Rh/10

$RhCl_3.3H_2O$ (0.5 mMole, 0.1346 g), sodium phenoxide (2.5 mMole, 0.2900 g), isoprene (0.5 Mole, 50 cm^3) and methanol (0.2 Mole, 8.2 cm^3)

were heated at 85° for 24 hours. Some decomposition occurred, giving a rhodium mirror on the walls of the ampoule. Fractionation of the product gave 1.7 g of dimers (bp 45-50°/5 mm). They were separated by preparative glc (Column A, 115° C, 60 cm^3/min.) and identified by nmr and ir spectra as XLV 30% and LI 70%. The main products of the reaction, however, were low boiling compounds which were not investigated, but which were presumably methyl isoprene-monomer ethers. Isoprene conversion to LI was only 3.5%.

6.4.3 Isoprene-Phenol Reactions

Expt. Rh/6

$RhCl(PPh_3)_3$ (0.5 mMole, 0.4626 g), sodium phenoxide (0.5 mMole, 0.0580 g), isoprene (0.1 Mole, 10 cm^3), phenol (0.2 Mole, 18.8 g) and benzene (35 cm^3) were heated at 85° for 24 hours. At the end of the reaction the solution was pale yellow; on exposure to air it gradually turned red. Glc analysis showed the presence of four main peaks, and a phenol conversion of 17% (i.e. an isoprene conversion of ~ 35% since almost all the product was composed of 1:1 adducts of phenol and isoprene). Fractional distillation of the product yielded (i) bp 35-80°, isoprene and benzene, (ii) bp 70-72°/10 mm phenol, 12.05 g, (iii) bp 57-60°/0.05 mm, o-subst. phenols, 2.93 g, (iv) bp 75-81°/0.05 mm, p-subst, phenols, 2.17 g. The substituted phenols were separated by preparative glc (Column A, 210°, 160 cm^3/min.) and characterised by nmr, ir and mass spectra as L, LII, LIII and LIV. They were formed in the ratios shown (analysis by glc and electronic integrator):

L	47%	LIII	40%
LII	10%	LIV	3%

Traces of disubstituted phenols were also obtained; the major component was isolated by preparative glc and on the basis of its nmr spectrum it was assigned the structure LV.

Expt. Rh/12

$RhCl(PPh_3)_3$ (0.5 mMole, 0.4626 g), sodium phenoxide (0.5 mMole, 0.0580 g), isoprene (0.5 Mole, 50 cm^3) and phenol (0.1 Mole, 9.4 g) were heated at 85° for 24 hours. In this reaction, the amount of disubstituted phenols obtained was about 3% of the product. Phenol conversion was estimated at 23% by glc analysis. The distribution of the monosubstituted phenols was somewhat different from that of Expt. Rh/6 :

L	58%	LIV	2%
LII	9%	LV + other disubst. phenols	3%
LIII	28%		

Expt. Rh/7

$Rh(nbd)_2BF_4$ (0.5 mMole, 0.1869 g), sodium phenoxide (0.5 mMole, 0.0580 g), isoprene (0.1 Mole, 10 cm^3), phenol (0.2 Mole, 18.8 g) and benzene (35 cm^3) were heated at 85° for 24 hours. No reaction occurred.

Expt. Rh/8

$RhCl_3.3H_2O$ (0.5 mMole, 0.1364 g), sodium phenoxide (0.5 mMole, 0.0580 g), isoprene (0.1 Mole, 10 cm^3), phenol 0.2 Mole, 18.8 g) and benzene (35 cm^3) were heated at 85° for 24 hours. No reaction occurred, the rhodium chloride did not dissolve at all, and appeared unchanged.

Expt. Rh/16

Sodium phenoxide (0.1 mMole, 0.0116 g), phenol (0.04 Mole, 3.76 g), isoprene (0.02 Mole, 2 cm^3) and benzene (10 cm^3) were heated at 85° for 24 hours in a 20 cm^3 ampoule. No products were observed by glc .

Expt. Rh/18

$RhCl_2(Pcy_3)_2$ (0.5mMole, 0.3669 g), sodium phenoxide (0.5 mMole, 0.0580 g), isoprene (0.1 Mole, 10 cm^3), phenol (0.2 Mole, 18.8 g) and benzene (35 cm^3) were heated at 85° for 24 hours. No reaction occurred.

Expt. Rh/20

$RhCl(PPh_3)_3$ (0.1 mMole, 0.0925 g), phenol (0.04 Mole, 3.76 g) isoprene (0.08 Mole, 8 cm^3) and benzene (8 cm^3) were heated at 85° for 24 hours in a 30 ml ampoule. No products were obtained. The solution was pale yellow.

6.4.4 Isoprene-Anisole Reaction

Expt. Rh/19

$RhCl(PPh_3)_3$ (0.5 mMole, 0.4626 g), sodium phenoxide (0.5 mMole, 0.0580 g), isoprene (0.1 Mole, 10 cm^3), anisole (0.2 Mole, 21.6 g) and benzene (35 cm^3) were heated at 85° for 24 hours. Glc revealed no products.

6.4.5 Butadiene-Phenol Reaction

Expt. Rh/15

$RhCl(PPh_3)_3$ (0.5 mMole, 0.4626 g), sodium phenoxide (0.5 mMole, 0.0580 g), butadiene (0.14 Mole, 6.15 g) phenol (0.2 Mole, 18.8 g) and benzene (40 cm^3) were heated at 85° for 24 hours. Phenol conversion was estimated at 20% from which butadiene conversion was calculated as 29%. Fractional distillation yielded (i) bp < 81% butadiene and benzene, (ii) bp 70-72°/10 mm, phenol, 14.8 g (iii) bp 62-64°/0.1 mm, o-subst. phenols 6.29 g (iv) bp 89-91°/0.15 mm, p-subst. phenols 4.32 g. From fractions (iii) and (iv) six substituted phenols were isolated by preparative glc (Column A, 210°, 140 ml/min.). Their structures were assigned by nmr and ir spectroscopy as LVI - LXI; glc analysis of the reaction mixture gave their proportions as shown:

LVI	2%	LIX	35%
LVII	23%	LX	<1%
LVIII	34%	LXI	6% .

SECTION B

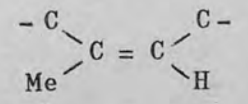
SPECTROSCOPIC DATA OF ORGANIC PRODUCTS

6.5 SPECTRAL DATA OF ORGANIC PRODUCTS

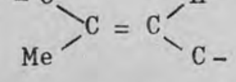
All ^{1}H nmr spectra were obtained from carbon tetrachloride solutions of the samples; tetramethylsilane was used as internal standard. The spectra were run on a Varian HA 100 or EM 360 spectrometer. Infrared spectra were obtained from the neat samples between KBr or NaCl plates on a Perkin Elmer 337 or Pye Unicam SP 1000 Spectrometer. Mass spectra (80 eV) were run on a Hitachi-Perkin Elmer MS 90 spectromer, with a glc link. Purified samples were injected on to the column (2 metre, 10% PEG 20 M on Celite) and the spectrum was scanned at the top of the sample peak.

Of the three spectroscopic methods used, ^{1}H nmr gave by far the most information. Infrared spectra were useful chiefly as confirmatory evidence, particularly in the case of the substituted phenols and the terpenoid alcohols, where a band at about 3500 cm^{-1} confirmed the presence of an -OH grouping. The C-H out-of-plane deformation vibrations of the vinyl $(-CH = CH_2)$ and vinylidene $(\gt C = CH_2)$ groups were also useful, but in the case of the trisubstituted double band $(\gt C = C{\diagup}^{H})$ were not reliable, being generally weak or even absent. Mass spectra were of use chiefly in determining the molecular weights of compounds and in establishing identities.

The configurations of products about tri-substituted double bonds were assigned by making use of the observation that the methyl group in a cis-type double bond (A) has a slightly higher (about 0.07 ppm) δ value than the methyl group in a trans-type double bond$^{(175)}$.



(A)



(B)

Where both isomers were available it was found that the isomer assigned the cis-structure by the above method had the shorter glc retention time; this is a well-known phenomenon. Where only one isomer was available, the configuration was assigned by comparison of chemical shifts with similar compounds.

The spectra data given in this Section are grouped as follows :

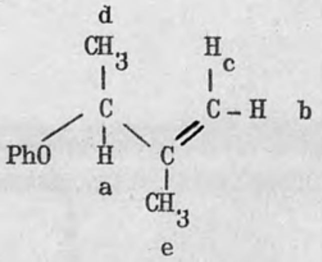
(i) Phenyl ethers ($PhOC_5H_9$)
(ii) Phenyl ethers ($PhOC_{10}H_{17}$)
(iii) Methyl and ethyl ethers ($MeOC_{10}H_{17}$ & $EtOC_{10}H_{17}$)
(iv) Isoprene dimers ($C_{10}H_{16}$)
(v) Substituted phenols.
(vi) Alcohols

The following abbreviations have been used :

s : singlet
d : doublet
t : triplet
q : quartet
m : multiplet

6.5.1 Phenyl Isoprene-Monomer Ethers (PhO C_5H_9)

XLVI 2-Methyl-3-phenoxy-but-1-ene



nmr (60 MHz)

δ		Assignment
4.64	(q, 1H)	a
4.8-5.0	(m, 2H)	b, c
1.42	(d, 3H)	d
1.73	(s, 3H)	e
6.6-7.3	(m, 5H)	phenyl protons

J_{ad} = 6.5 Hz.

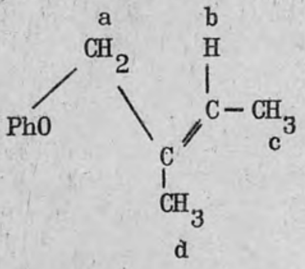
Infrared

690 cm^{-1} (strong), 755 cm^{-1} (strong) : mono-substituted benzene ring

885 cm^{-1} (medium) : $>C = CH_2$

1240 cm^{-1} (strong) : $Ph - O - C\langle -$

XLVII 1-Phenoxy-2-methyl-trans-but-2-ene



nmr (60 MHz)

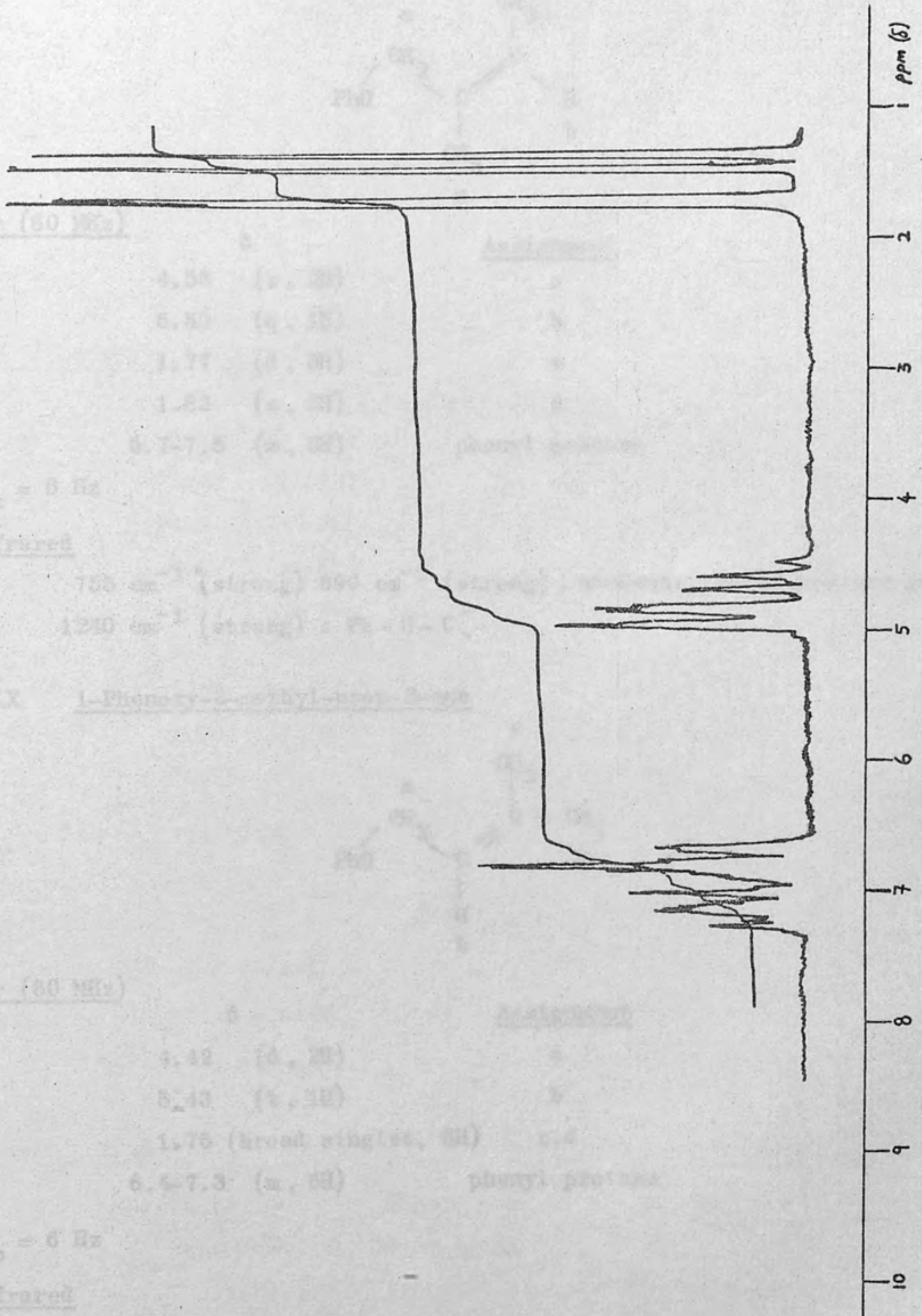
δ		Assignment
4.30	(s, 2H)	a
5.67	(q, 1H)	b
1.64	(d, 3H)	c
1.72	(s, 3H)	d
6.6-7.3	(m, 5H)	phenyl protons

J_{bc} = 7 Hz

Infrared

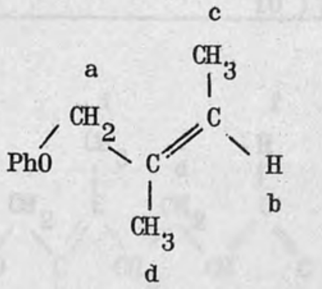
690 cm^{-1} (strong), 755 cm^{-1} (strong) : mono-substituted benzene ring

1240 cm^{-1} (strong) : $Ph - O - C\langle -$



60 MHz 'H nmr SPECTRUM OF XLVI

XLVIII 1-Phenoxy-2-methyl-cis-but-2-ene



nmr (60 MHz)

δ		Assignment
4.53	(s, 2H)	a
5.50	(q, 1H)	b
1.77	(d, 3H)	c
1.83	(s, 3H)	d
6.7-7.5	(m, 5H)	phenyl protons

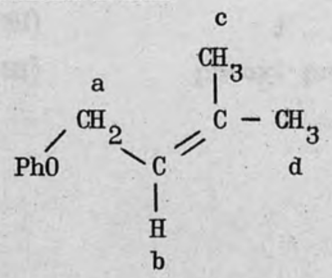
$J_{bc} = 6$ Hz

Infrared

755 cm^{-1} (strong) 690 cm^{-1} (strong) : monosubstituted benzene ring

1240 cm^{-1} (strong) : Ph - O - C< -

XLIX 1-Phenoxy-3-methyl-prop-2-ene



nmr (60 MHz)

δ		Assignment
4.42	(d, 2H)	a
5.43	(t, 1H)	b
1.75	(broad singlet, 6H)	c,d
6.4-7.3	(m, 5H)	phenyl protons

$J_{ab} = 6$ Hz

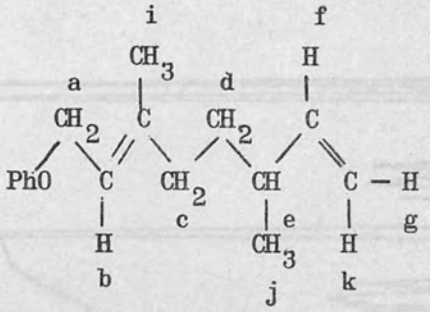
Infrared

695 cm^{-1} (strong), 755 cm^{-1} (strong) : monosubstituted benzene ring

1240 cm^{-1} (strong) : Ph - O - C< -

6.5.2 Phenyl Isoprene-Dimer Ethers ($PhOC_{10}H_{17}$)

XXIV



nmr (100 MHz)

δ	Assignment
4.44 (d, 2H)	a
5.43 (t, 1H)	b
1.94–2.22 (m, 3H)	c, e
1.3–1.6 (m, 2H)	d
5.63 (m, 1H)	f
4.8–5.0 (m, 2H)	g, h
1.70 (s, 3H)	i
1.00 (d, 3H)	j
6.6–7.3 (m, 5H)	phenyl protons

$J_{ab} = 7\,Hz$; $J_{ej} = 6\,Hz$

Infrared

800 cm^{-1} (weak) : $- CH = C\langle$

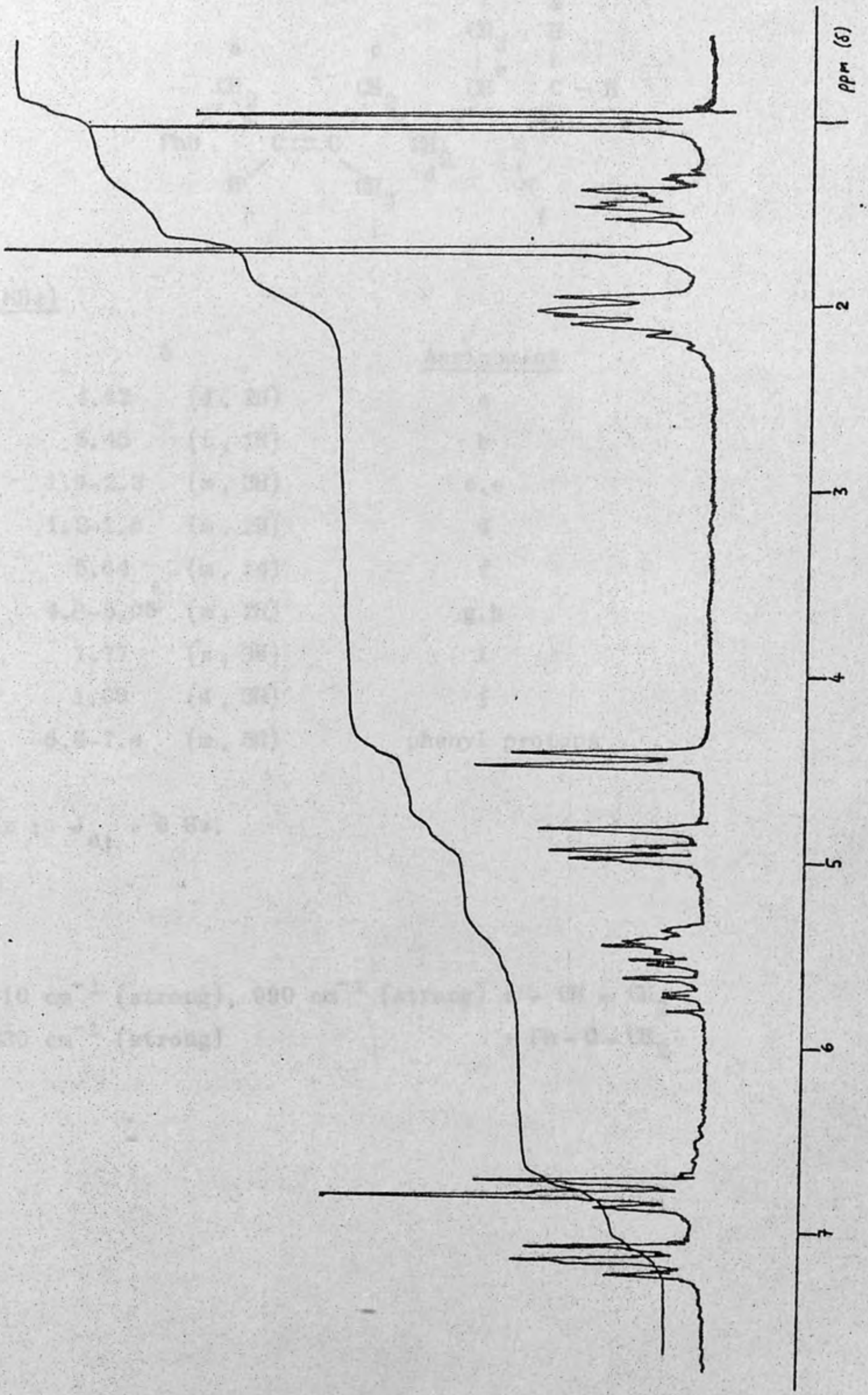
910 cm^{-1} (strong), 985 cm^{-1} (strong) : $- CH = CH_2$

1230 cm^{-1} (strong) : $Ph - O - CH_2 -$

Mass Spectrum

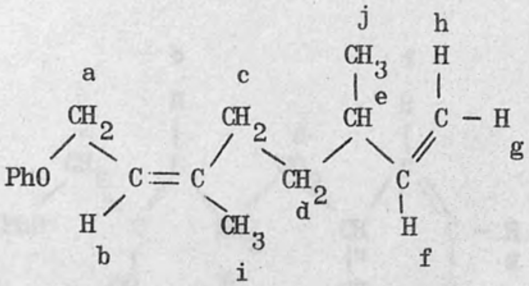
Molecular ion : m+/e = 230

base peak : m+/e = 81



100 MHz ¹H nmr SPECTRUM OF XXIV

XXV



nmr (100 MHz)

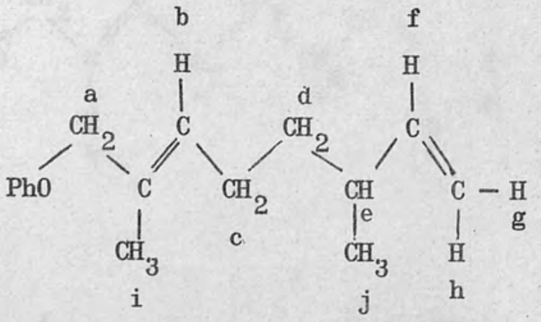
δ		Assignment
4.42	(d , 2H)	a
5.40	(t , 1H)	b
1.9-2.3	(m , 3H)	c, e
1.2-1.6	(m , 2H)	d
5.64	(m , 14)	f
4.8-5.05	(m , 2H)	g, h
1.77	(s , 3H)	i
1.00	(d , 3H)	j
6.6-7.4	(m , 5H)	phenyl protons

J_{ab} = 7 Hz ; J_{ej} = 6 Hz.

Infrared

910 cm^{-1} (strong), 990 cm^{-1} (strong) : $-CH=CH_2$
1230 cm^{-1} (strong) : $Ph-O-CH_2-$

XXVI



nmr (100 MHz)

δ		Assignment
4.33	(s , 2H)	a
5.44	(t , 1H)	b
1.9-2.25	(m , 3H)	c, e
1.3-1.6	(m , 2H)	d
5.64	(m , 1H)	f
4.8-5.1	(m , 2H)	g,h
1.72	(s , 3H)	i
1.00	(d , 3H)	j
6.6-7.4	(m , 5H)	phenyl protons

$J_{bc} = 7$ Hz ; $J_{ej} = 6$ Hz.

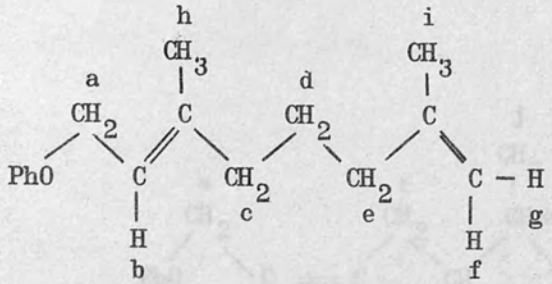
Infrared

810 cm^{-1} (weak) : $- CH = C\langle$

910 cm^{-1} (strong) , 990 cm^{-1} (strong) : $- CH = CH_2$

1230 cm^{-1} (strong) : $Ph - O - CH_2 -$

XXVII



nmr (100 MHz)

δ		Assignment
4.45	(d , 2H)	a
5.43	(t , 1H)	b
1.88–2.1	(m , 4H)	c, e
1.4–1.5	(m , 2H)	d
4.63	(s , 2H)	f, g
1.69	(s , 6H)	h, i
6.7–7.3	(m , 5H)	phenyl protons

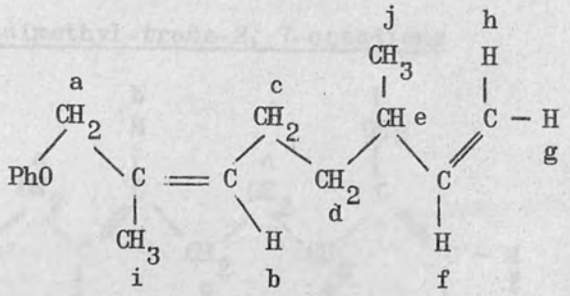
Infrared

820 cm^{-1} (weak) : $>C = CH_2$

885 cm^{-1} (strong) : $>C = CH_2$

1235 cm^{-1} (strong) : $Ph-O-CH_2-$

XXVIII



nmr (100 MHz)

δ		Assignment
4.43	(s , 2H)	a
5.33	(t , 1H)	b
1.9-2.3	(m , 4H)	c, e (?)
1.2-1.7	(m , 6H)	d (?)
5.64	(m , 1H)	f
4.8-5.1	(m , 4H)	g, h (?)
1.81	(s , 3H)	i
1.00	(d , 5H)	j (?)
6.6-7.3	(m , 7H)	phenyl protons (?)

It seems evident from the integration that the sample used in obtaining this spectrum was a mixture of at least two compounds. However the main features of the spectrum were very similar to those of the spectrum of XXVI, and it seems probable that XXVIII is the cis-isomer of XXVI.

Infrared

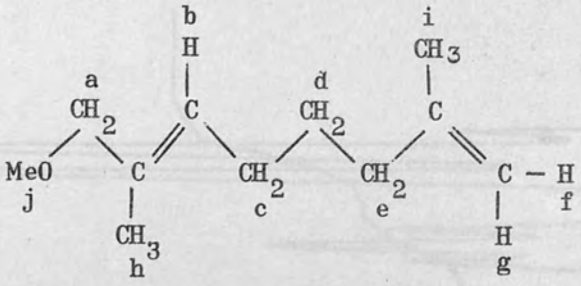
815 cm^{-1} (weak) : $C = CH -$
905 cm^{-1} (strong), 985 cm^{-1} (strong) : $- CH = CH_2$
1230 cm^{-1} (strong) : $Ph - O - CH_2 -$

Mass Spectrum

Molecular ion at m+/e = 230, as required for $C_{16}H_{22}O$. The base peak occurred at m+/e = 81.

6.5.3 Methyl and Ethyl Isoprene-Dimer Ethers

XXXIV 1-Methoxy-2.7-dimethyl-trans-2, 7-octadiene



nmr

δ		Assignment
3.67	(s , 2H)	a
5.30	(t , 1H)	b
1.85-2.2	(m , 4H)	c, e
1.5	(m , 2H)	d
4.63	(s , 2H)	f,g
1.58	(s , 3H)	h
1.68	(s , 3H)	i
3.11	(s , 3H)	j

J_{bc} = 7 Hz.

Infrared

850 cm^{-1} (weak) : $-CH=C<$

885 cm^{-1} (strong) $>C=CH_2$

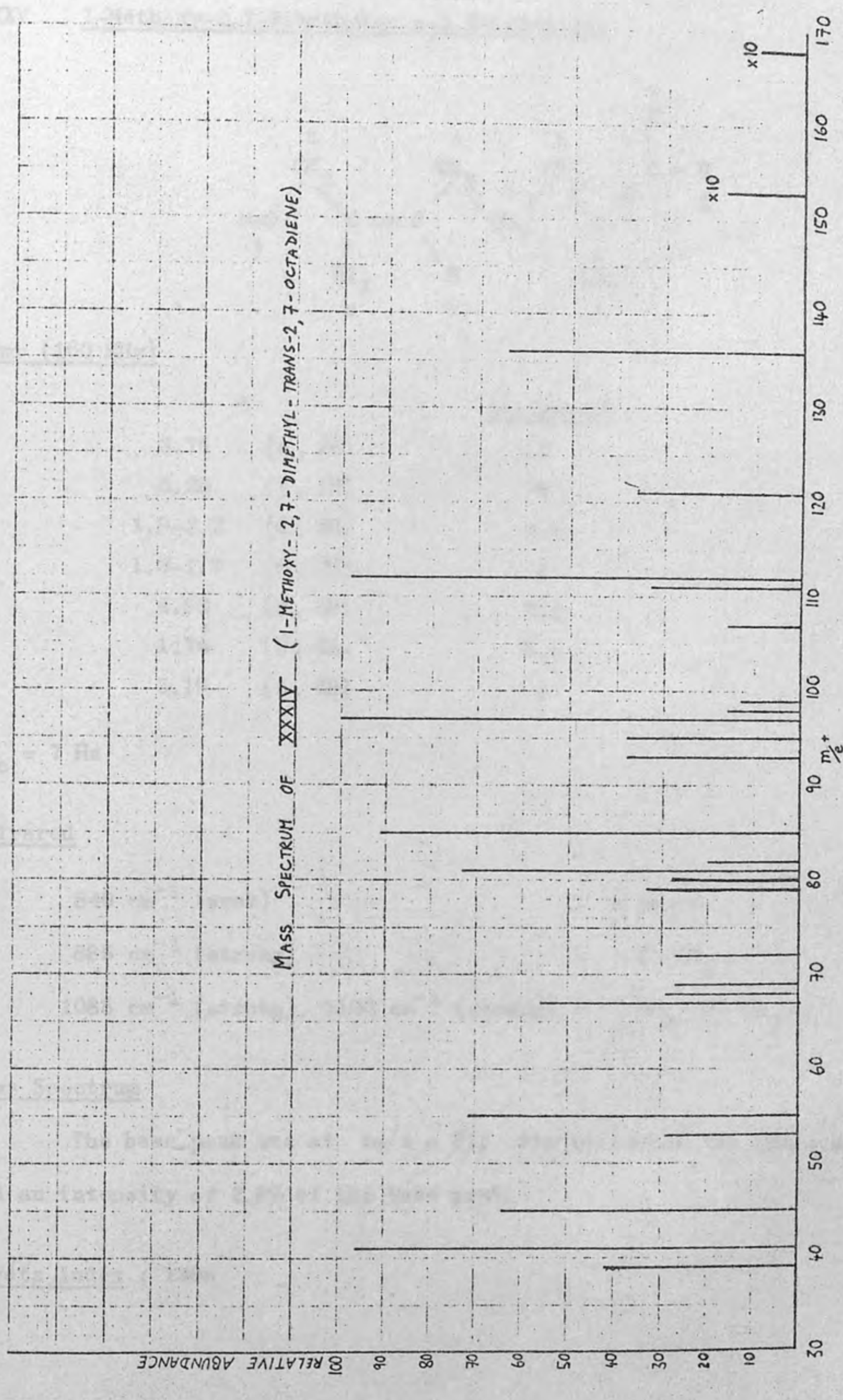
1092 cm^{-1} (strong) , 1112 cm^{-1} (strong) : $H_3C-O-CH_2-$

Mass Spectrum

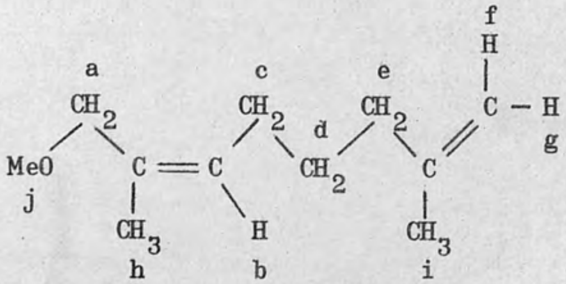
The mass spectrum had m+/e = 168, consistent with $C_{11}H_{20}O$. The base peak occurred at m+/e = 97.

Kováts Index : 1424.

100MHz ^{1}H nmr SPECTRUM OF XXXIV


MASS SPECTRUM OF XXXIV (1-METHOXY-2,7-DIMETHYL-TRANS-2,7-OCTADIENE)

XXXV 1-Methoxy-2,7-dimethyl-cis-2,7-octadiene



nmr (100 MHz)

δ		Assignment
3.79	(s , 24)	a
5.25	(t , 1H)	b
1.8-2.2	(m , 4H)	c, e
1.3-1.7	(m , 2H)	d
4.62	(s , 2H)	f, g
1.70	(s , 6H)	h, i
3.19	(s , 3H)	j

J_{bc} = 7 Hz

Infrared

840 cm^{-1} (weak) : $- CH = C$

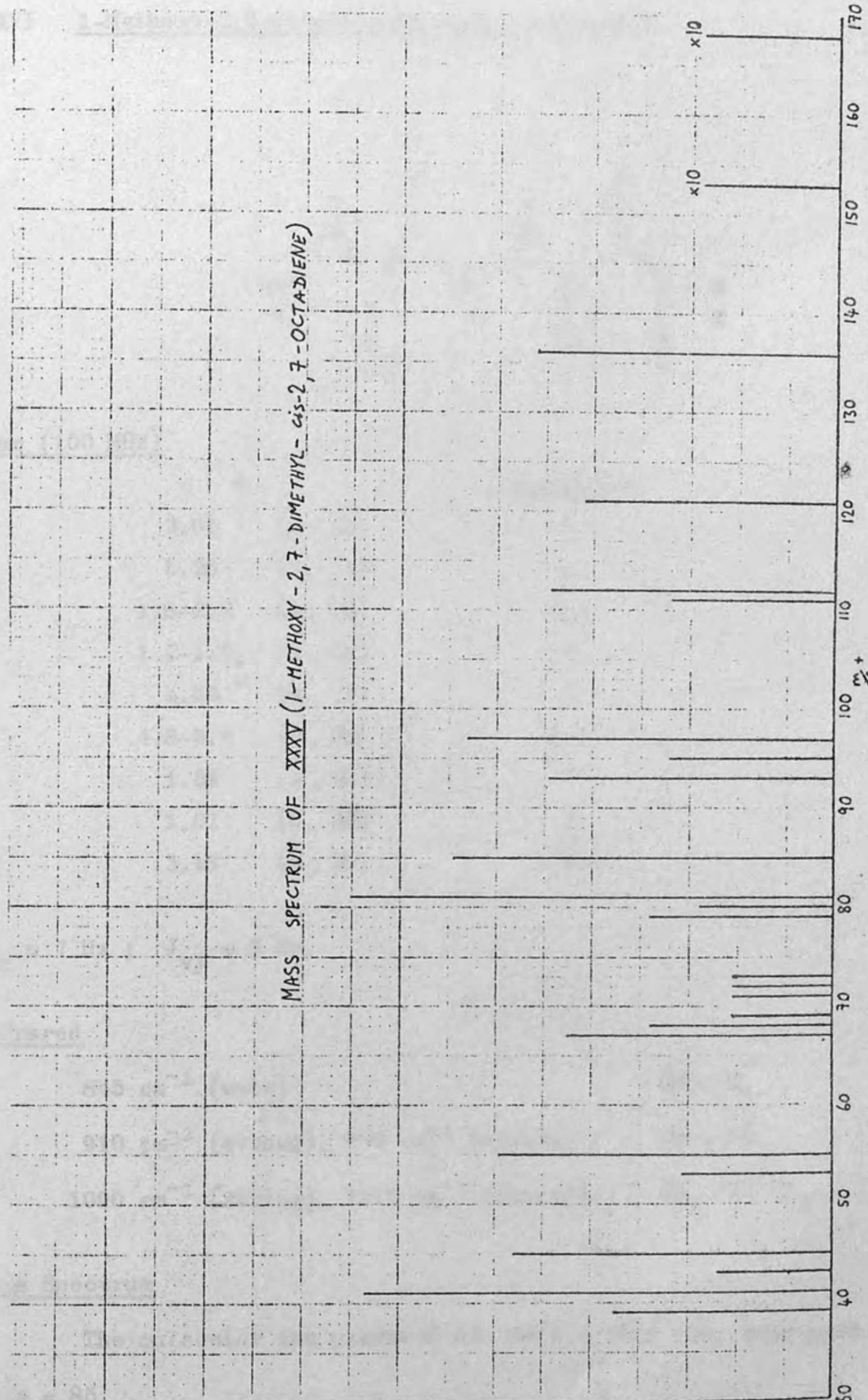
885 cm^{-1} (strong) : $C = CH_2$

1085 cm^{-1} (strong), 1100 cm^{-1} (strong) : $CH_3 - O - CH_2 -$

Mass Spectrum

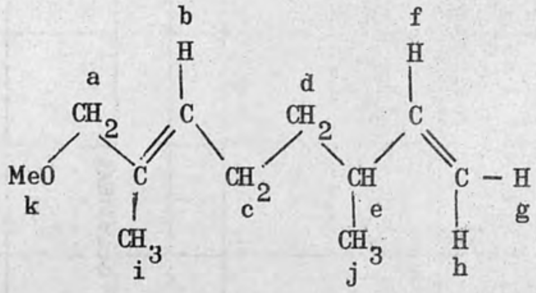
The base peak was at m+/e = 81; the molecular ion (M+/e = 168) had an intensity of 2.8% of the base peak.

Kováts Index : 1398



MASS SPECTRUM OF XXXV (1-METHOXY-2,7-DIMETHYL-cis-2,7-OCTADIENE)

XXXVI 1-Methoxy-2,6-dimethyl-trans-2,7-octadiene



nmr (100 MHz)

δ		Assignment
3.66	(s , 2H)	a
5.26	(t , 1H)	b
1.8-2.2	(m , 3H)	c, e
1.2-1.5	(m , 2H)	d
5.63	(m , 1H)	f
4.8-5.0	(m , 2H)	g,h
1.59	(s , 3H)	i
1.01	(d , 3H)	j
3.18	(s , 3H)	k

$J_{bc} = 7$ Hz ; $J_{ej} = 6$ Hz.

Infrared

845 cm^{-1} (weak) : $-\mathrm{CH}=\mathrm{C}\langle$

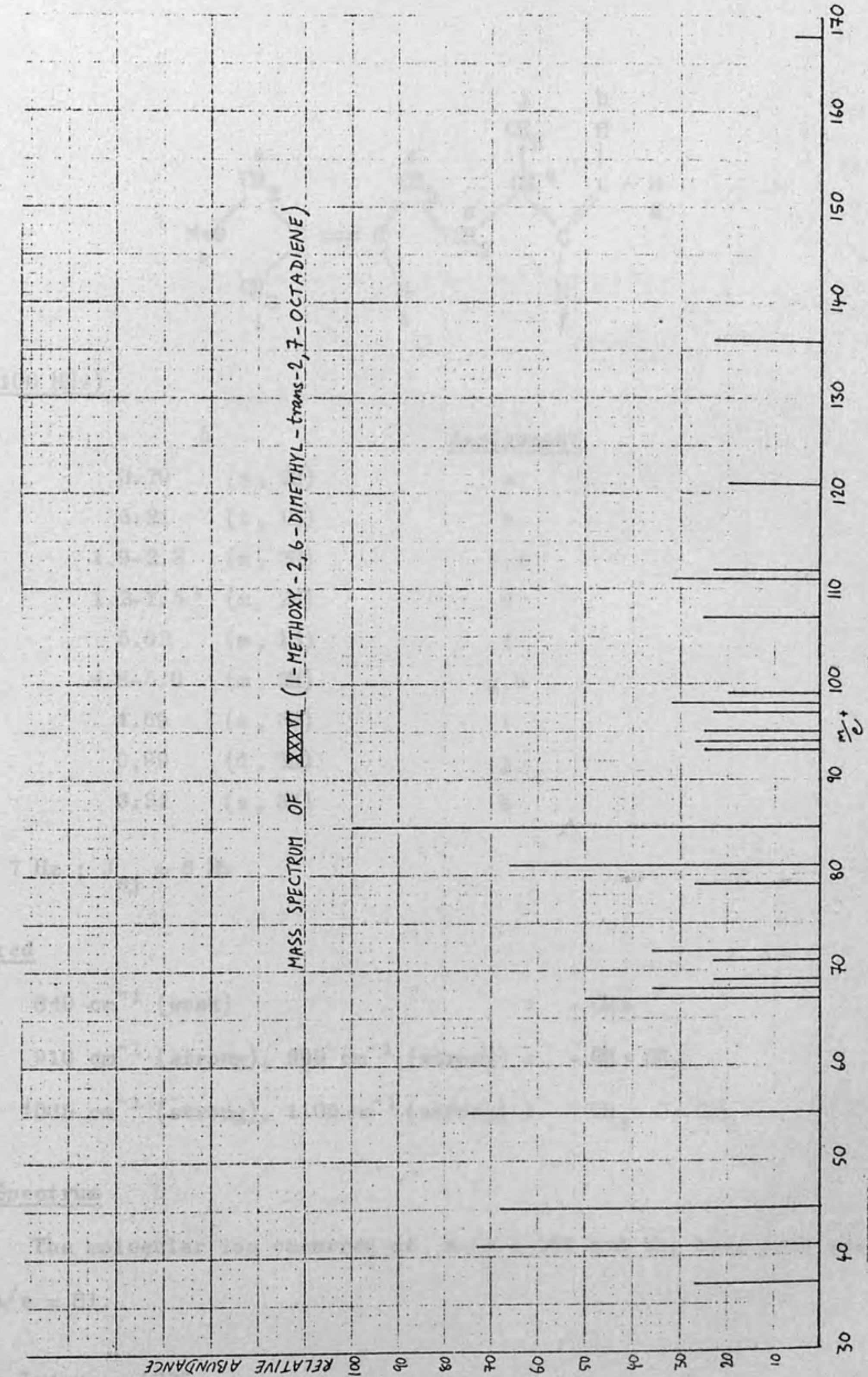
910 cm^{-1} (strong), 990 cm^{-1} (strong) : $\mathrm{CH}=\mathrm{CH_2}$

1090 cm^{-1} (strong), 1110 cm^{-1} (strong): $\mathrm{CH_3-O-CH_2-}$

Mass Spectrum

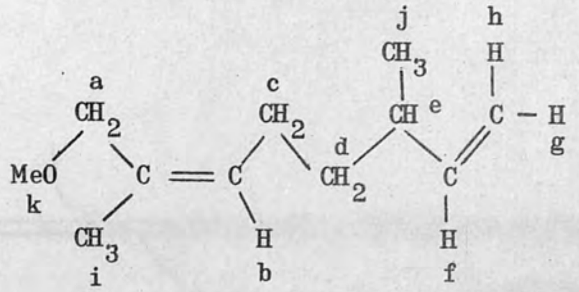
The molecular ion occurred at m+/e ≃ 168; the base peak was at m+/e = 85.

Kováts Index : 1368.



MASS SPECTRUM OF XXXVI (1-METHOXY-2,6-DIMETHYL-trans-2,7-OCTADIENE)

XXXVII 1-Methoxy-2,6-dimethyl-cis-2,7-octadiene



nmr (100 MHz)

δ		Assignment
3.79	(s , 2H)	a
5.21	(t , 1H)	b
1.9–2.3	(m , 3H)	c, e
1.2–1.5	(m, 2H)	d
5.62	(m , 1H)	f
4.8–5.0	(m , 2H)	g, h
1.69	(s , 3H)	i
0.99	(d , 3H)	j
3.22	(s , 3H)	k

$J_{bc} = 7$ Hz ; $J_{ej} = 6$ Hz

Infrared

840 cm^{-1} (weak) : $-CH=C\langle$

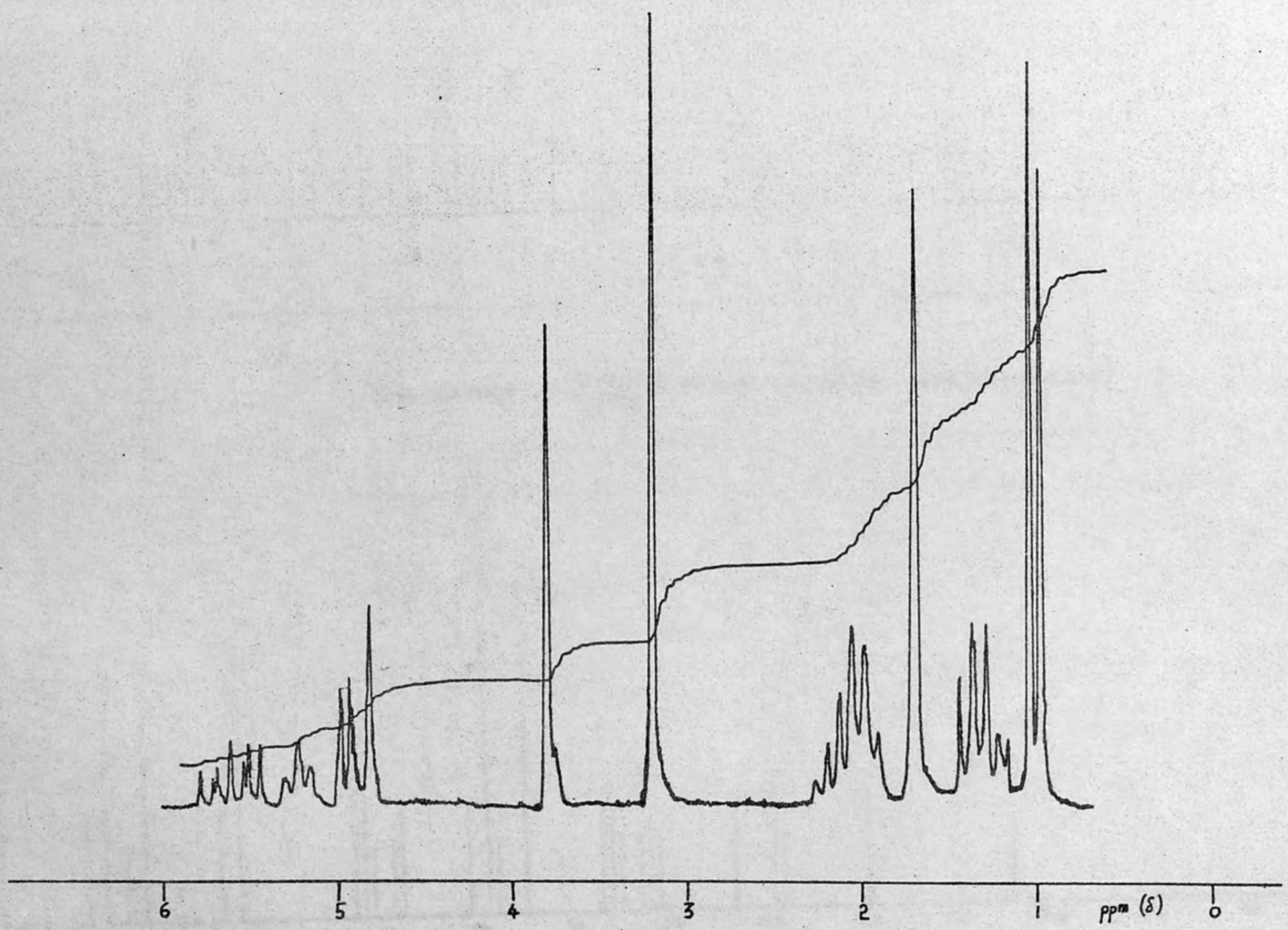
910 cm^{-1} (strong), 990 cm^{-1} (strong) : $-CH=CH_2$

1085 cm^{-1} (strong), 1105 cm^{-1} (strong) : CH_3-O-CH_2-

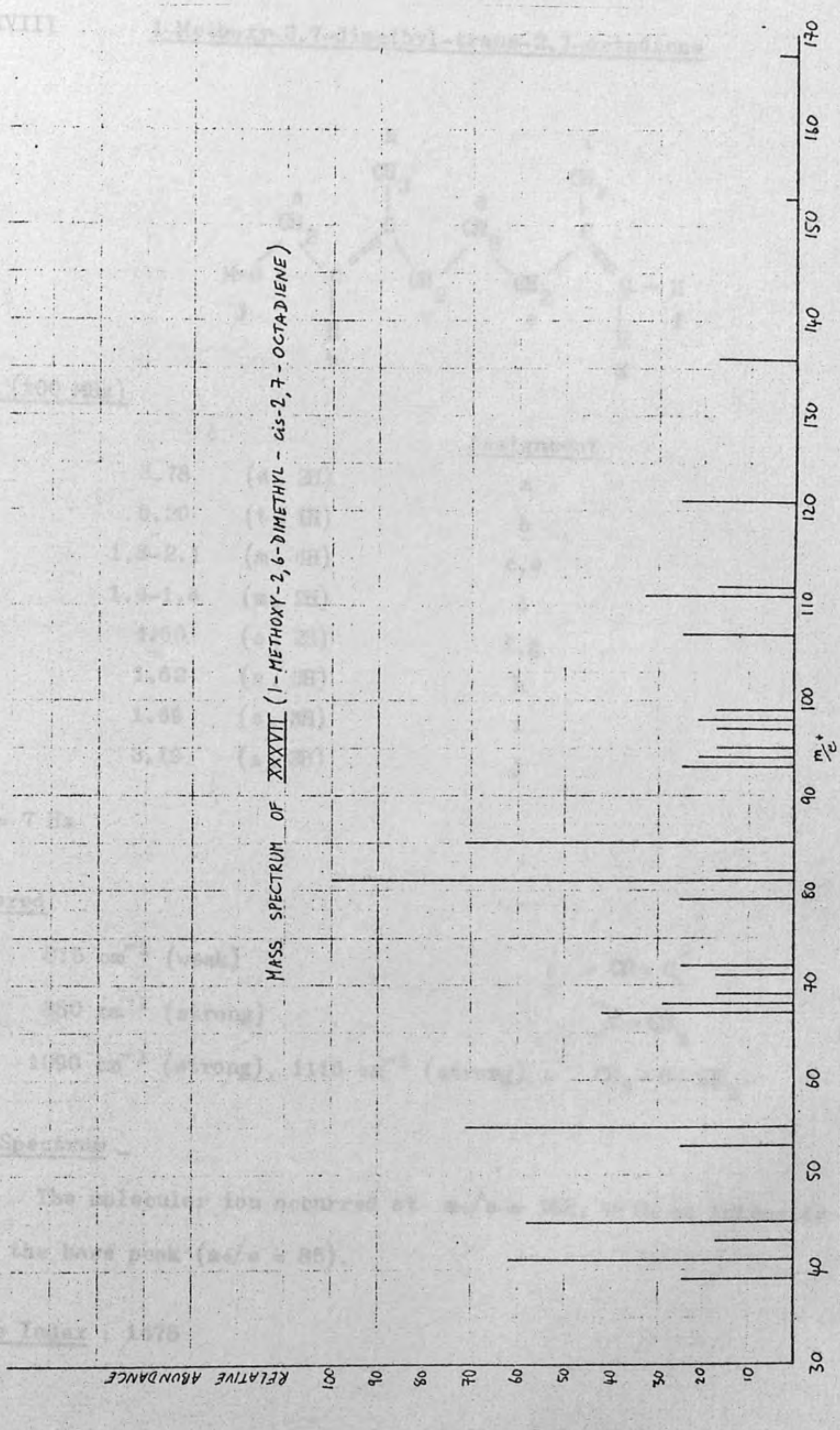
Mass Spectrum

The molecular ion occurred at m+/e = 168 and the base peak was at m+/e = 81.

Kovats Index : 1336.

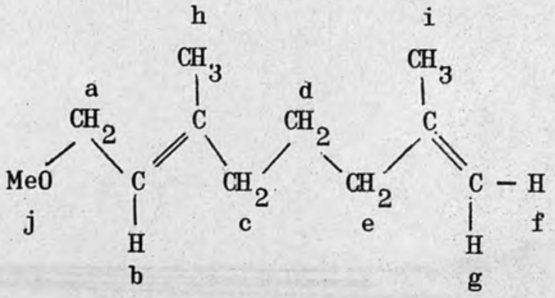


100 MHz ^{1}H nmr SPECTRUM OF XXXVII



MASS SPECTRUM OF XXXVII (1-METHOXY-2,6-DIMETHYL - cis-2,7-OCTADIENE)

XXXVIII 1-Methoxy-3,7-dimethyl-trans-2,7-octadiene



nmr (100 MHz)

δ		Assignment
3.78	(d , 2H)	a
5.20	(t , 1H)	b
1.8-2.1	(m , 4H)	c, e
1.4-1.6	(m , 2H)	d
4.60	(s , 2H)	f, g
1.62	(s , 3H)	h
1.69	(s , 3H)	i
3.19	(s , 3H)	j

J_{ab} = 7 Hz

Infrared

815 cm^{-1} (weak) : $-CH=C<$

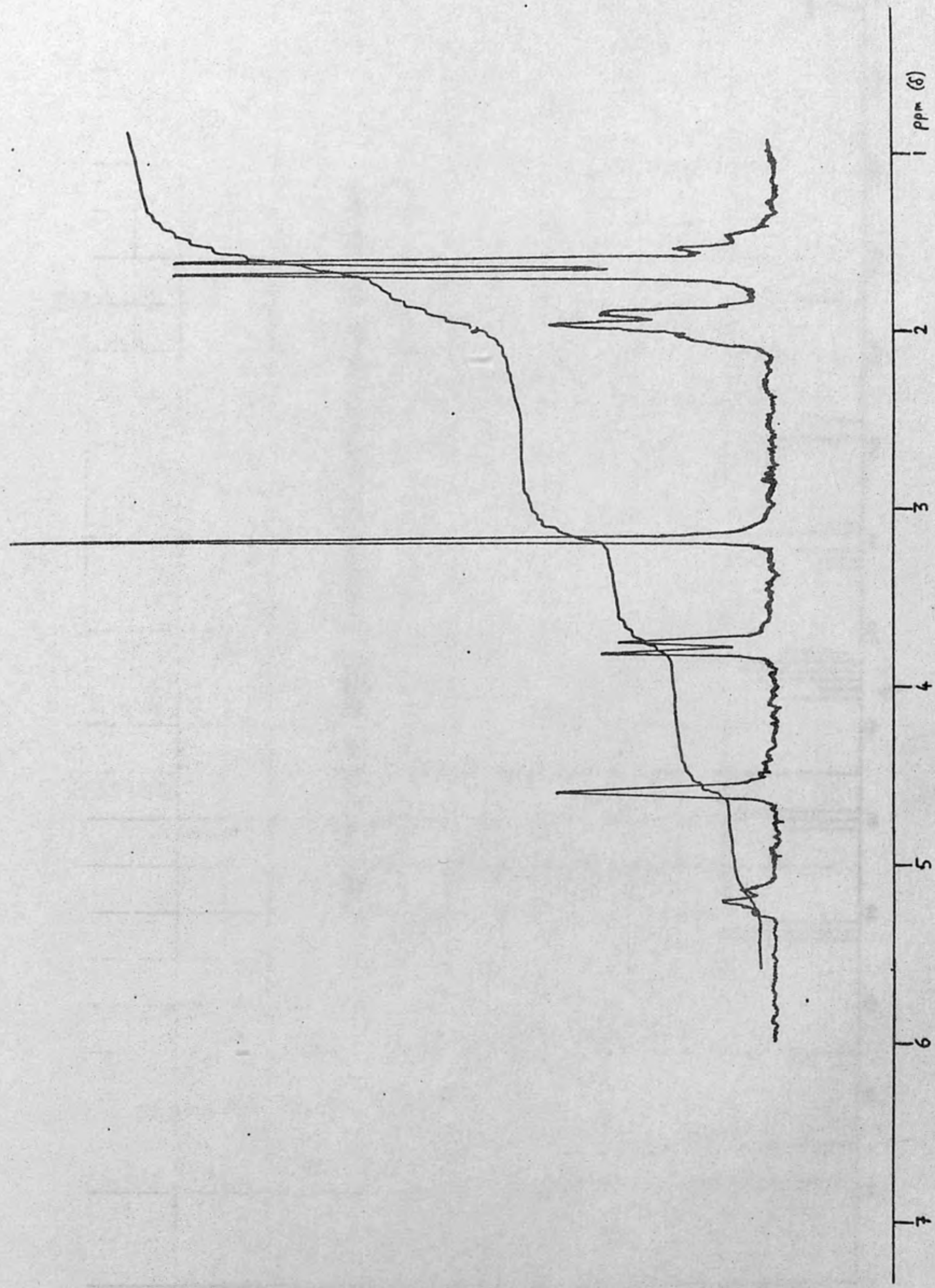
880 cm^{-1} (strong) $>C=CH_2$

1090 cm^{-1} (strong), 1110 cm^{-1} (strong) : CH_3-O-CH_2-

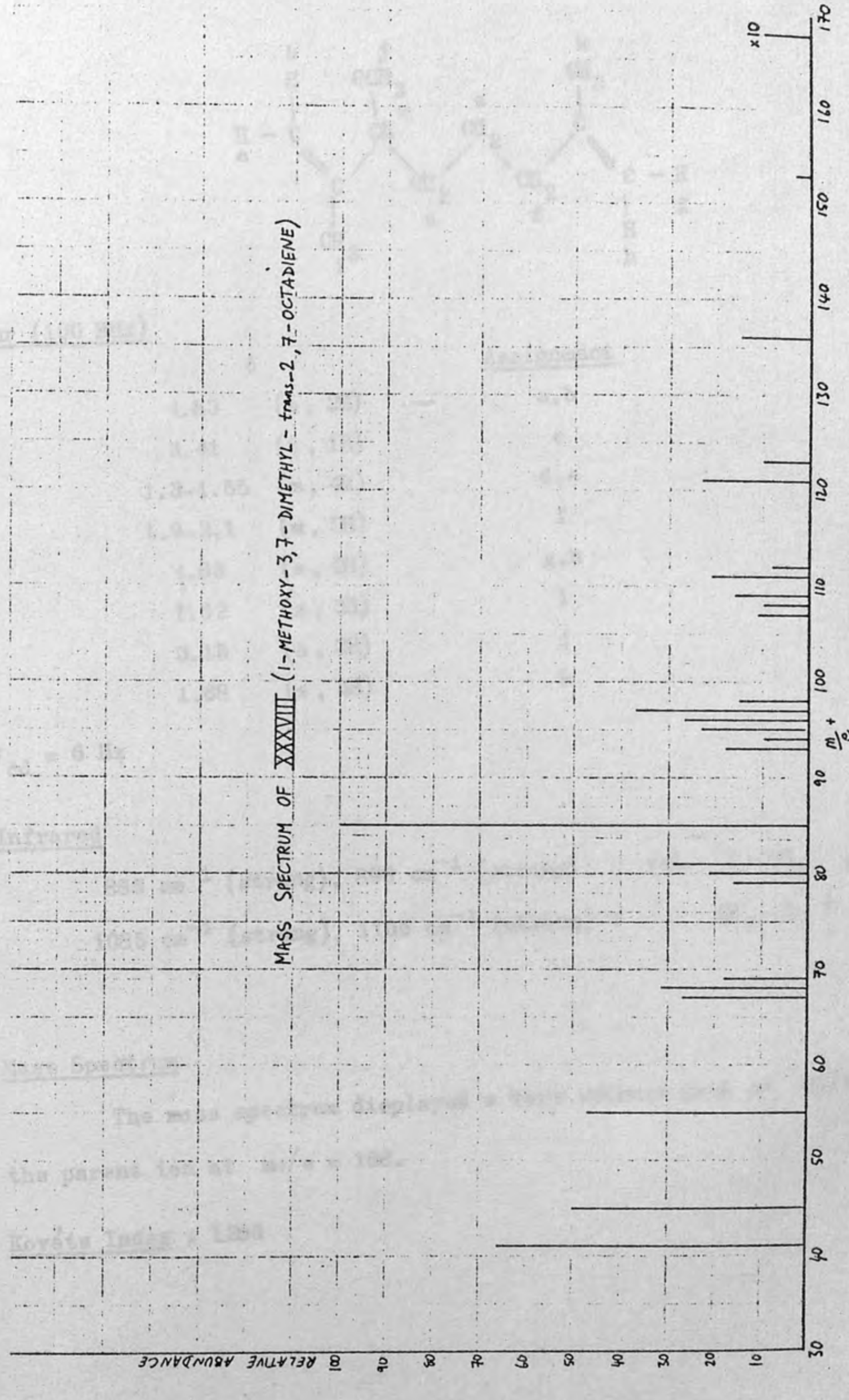
Mass Spectrum

The molecular ion occurred at m+/e = 168, with an intensity of 1% of the base peak (m+/e = 85).

Kováts Index : 1475

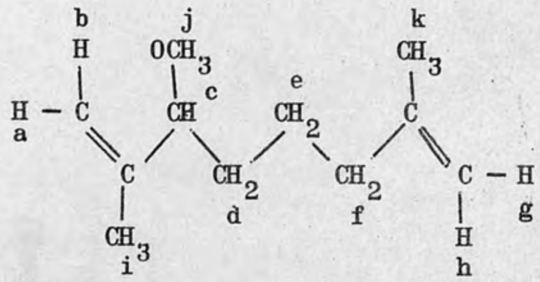


100MHz ^{1}H nmr SPECTRUM OF XXXVIII



MASS SPECTRUM OF XXXVIII (1-METHOXY-3,7-DIMETHYL-*trans*-2,7-OCTADIENE)

XXXIX 3-Methoxy-2,7-dimethyl-1,7-octadiene



nmr (100 MHz)

δ		Assignment
4.83	(s , 2H)	a,b
3.41	(t , 1H)	c
1.3-1.55	(m , 4H)	d,e
1.9-2.1	(m , 2H)	f
4.63	(s , 2H)	g,h
1.62	(s , 3H)	i
3.15	(s , 3H)	j
1.68	(s , 3H)	k

$J_{cd} = 6$ Hz

Infrared

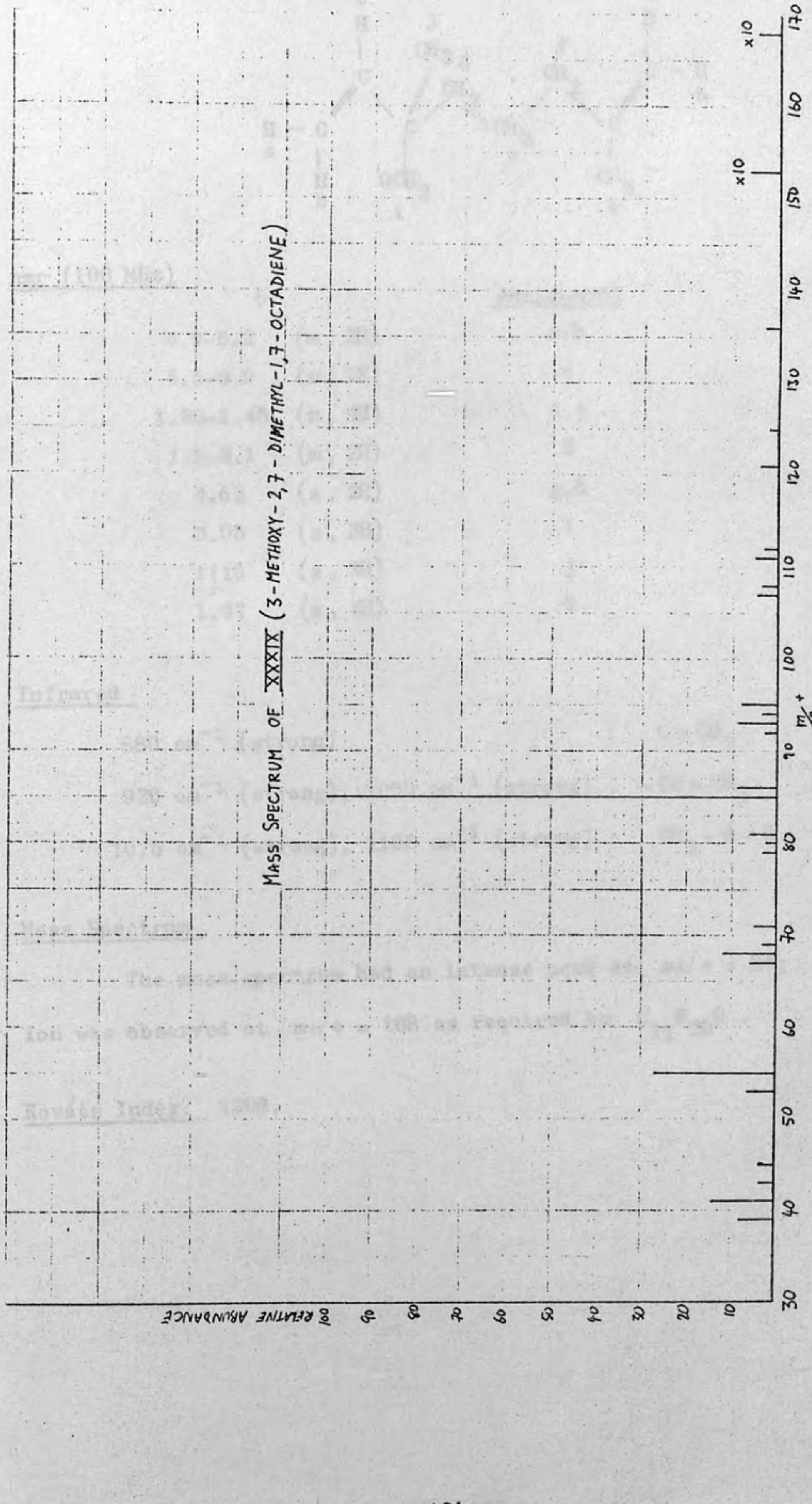
885 cm^{-1} (strong), 898 cm^{-1} (strong) : two $>C=CH_2$ groups

1085 cm^{-1} (strong), 1105 cm^{-1} (strong) : $CH_3-O-\overset{|}{\underset{|}{C}}-$

Mass Spectrum

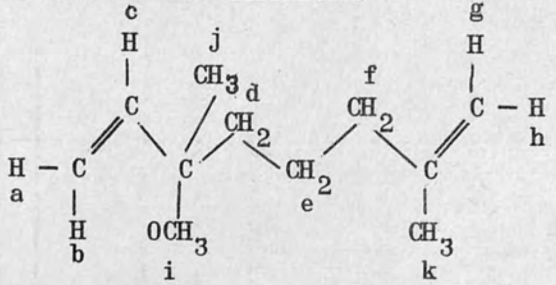
The mass spectrum displayed a very intense peak at m+/e = 85 and the parent ion at m+/e = 168.

Kováts Index : 1263



MASS SPECTRUM OF XXXIX (3-METHOXY-2,7-DIMETHYL-1,7-OCTADIENE)

XL 3-Methyl-3,7-dimethyl-1,7-octadiene



nmr (100 MHz)

δ		Assignment
4.9-5.2	(m, 2H)	a,b
5.5-5.9	(m, 1K)	c
1.35-1.45	(m, 4H)	d,e
1.8-2.1	(m, 2H)	f
4.62	(s, 2H)	g,h
3.05	(s, 3H)	i
1.16	(s, 3H)	j
1.67	(s, 3H)	k

Infrared

880 cm^{-1} (strong) : $C=CH_2$

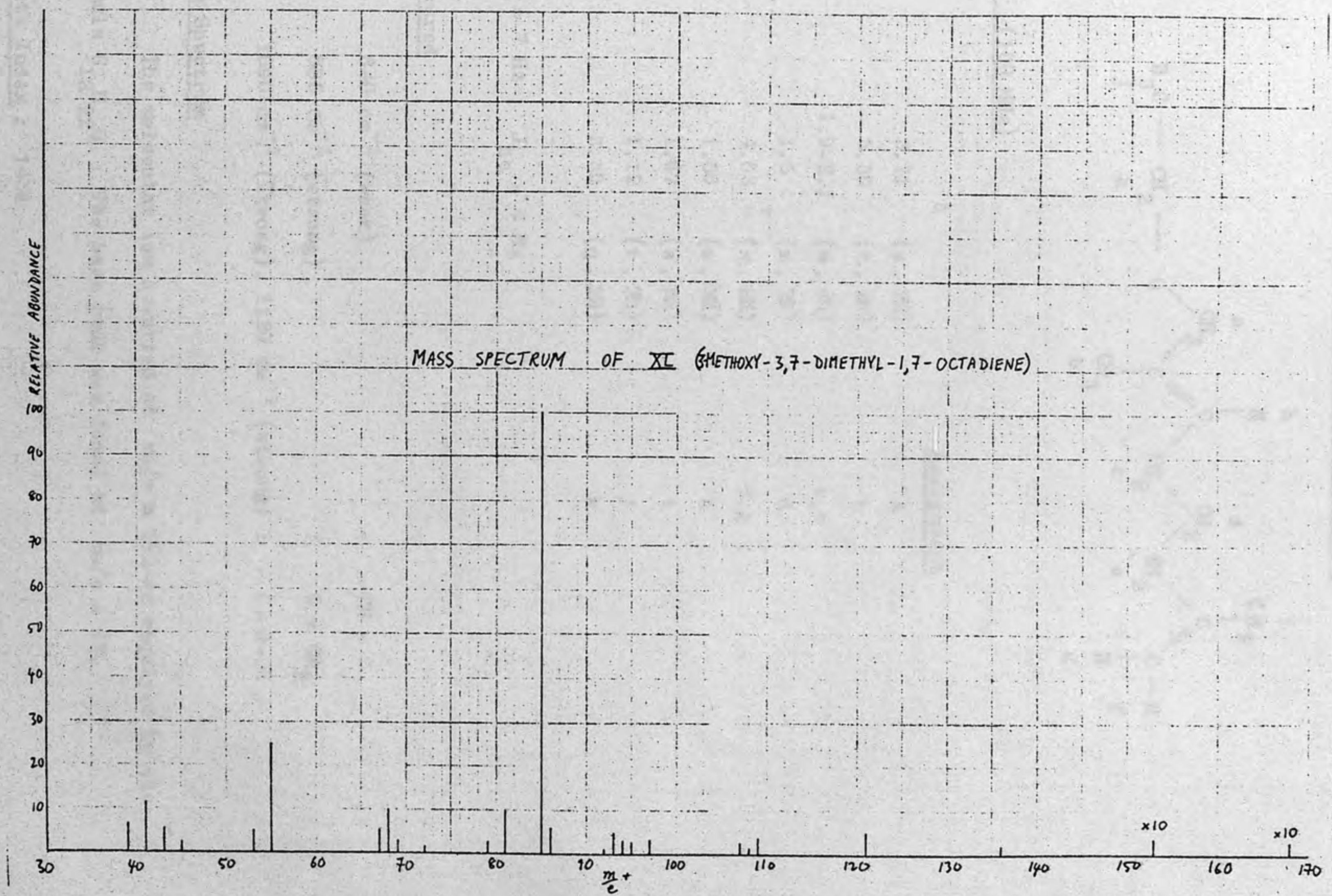
920 cm^{-1} (strong), 1000 cm^{-1} (strong) : $-CH=CH_2$

1075 cm^{-1} (strong), 1105 cm^{-1} (strong) : CH_3-O-C-

Mass Spectrum

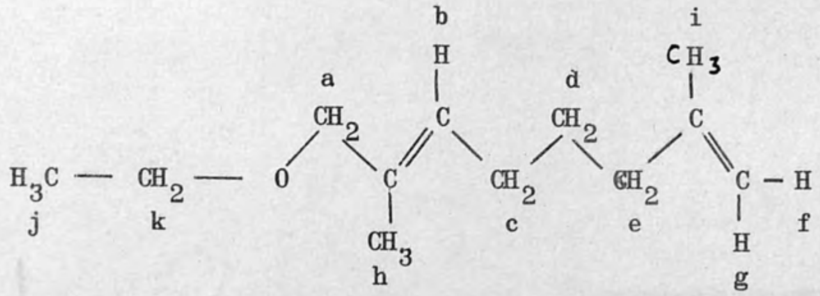
The mass spectrum had an intense peak at m+/e = 85; the parent ion was observed at m+/e = 168 as required by $C_{11}H_{20}O$.

Kováts Index: 1308.



MASS SPECTRUM OF XL (3METHOXY-3,7-DIMETHYL-1,7-OCTADIENE)

XLII 1-Ethoxy-2,7-dimethyl-trans-2,7-octadiene



nmr (100 MHz)

δ		Assignment
3.71	(s , 2H)	a
5.30	(t , 1H)	b
1.9-2.1	(m , 4H)	c, e
1.5	(m , 2H)	d
4.63	(s , 2H)	f, g
1.56	(s , 3H)	h
1.67	(s , 3H)	i
1.12	(t , 3H)	j
3.30	(q , 2H)	k

J_{jk} = 7 Hz ; J_{bc} = 7 Hz

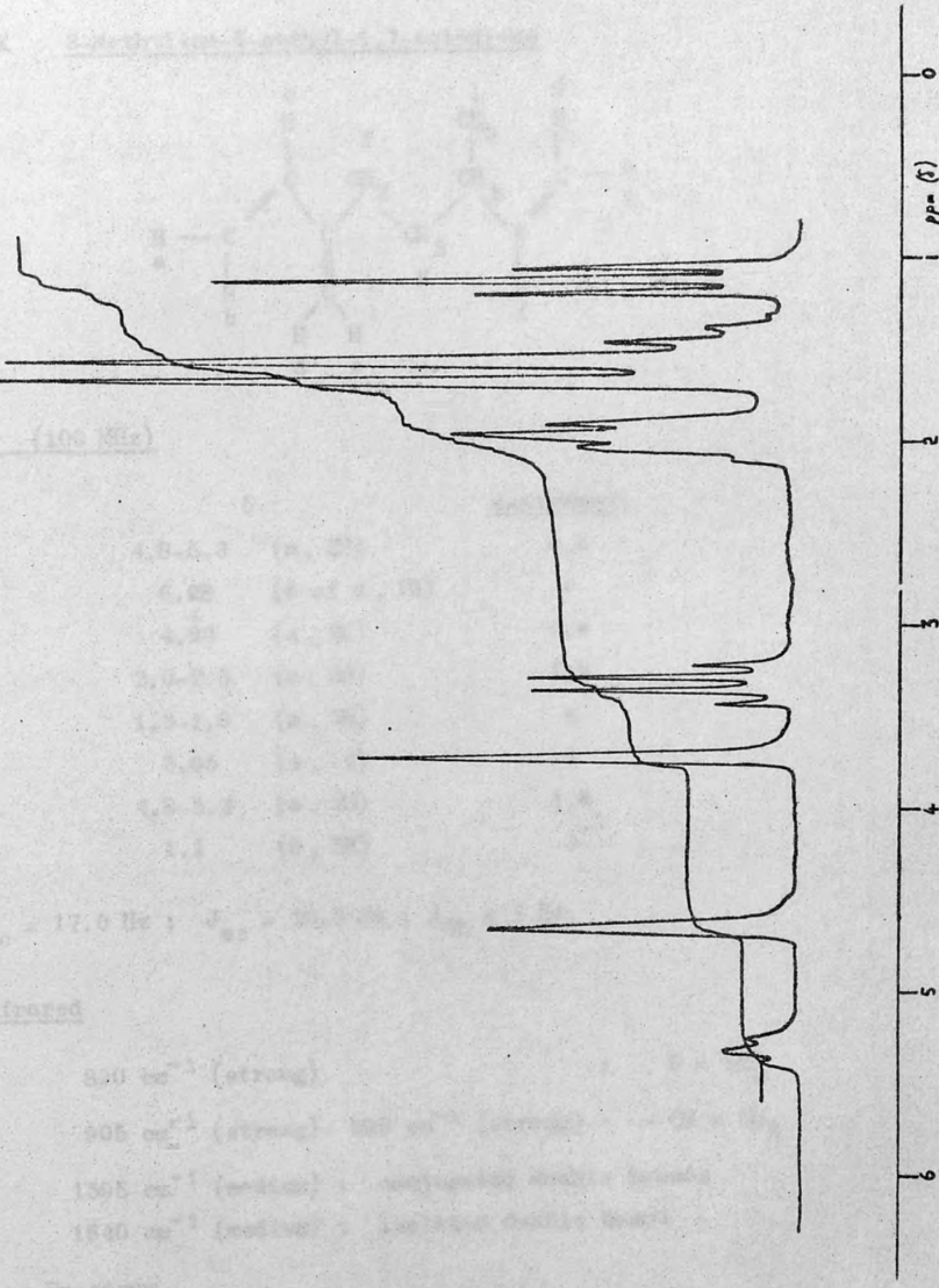
Infrared

840 cm^{-1} (weak)	: – CH = C
885 cm^{-1} (strong)	: C = CH_2
1090 cm^{-1} (strong), 1120 cm^{-1} (strong)	: – C – O – C –

Mass Spectrum

The molecular ion occurred at m+/e ≧ 182 as required by the formula $C_{12}H_{22}O$. The base peak was found at m+/e = 43.

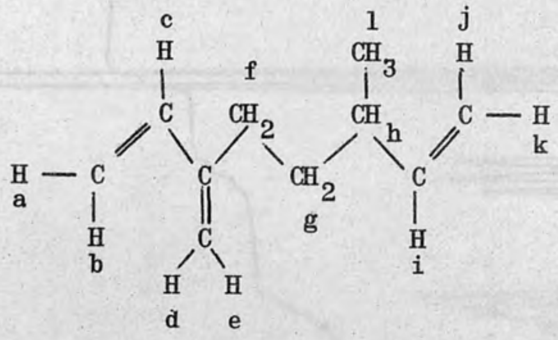
Kováts Index : 1459



100MHz 'H nmr SPECTRUM OF XLII

6.5.4 $C_{10}H_{16}$ Hydrocarbon

XXIX 3-Methylene-6-methyl-1,7-octadiene



nmr (100 MHz)

δ		Assignment
4.8-5.3	(m , 2H)	a,b
6.28	(d of d , 1H)	c
4.93	(s , 2H)	d,e
2.0-2.3	(m , 3H)	f,h
1.3-1.6	(m , 2H)	g
5.65	(m , 14)	i
4.8-5.3	(m , 2H)	j,k
1.1	(d , 3H)	l

$J_{bc} = 17.5$ Hz ; $J_{ac} = 10.5$ Hz ; $J_{dh} = 7$ Hz

Infrared

890 cm^{-1} (strong) : C = CH_2

905 cm^{-1} (strong) 990 cm^{-1} (strong) : - CH = CH_2

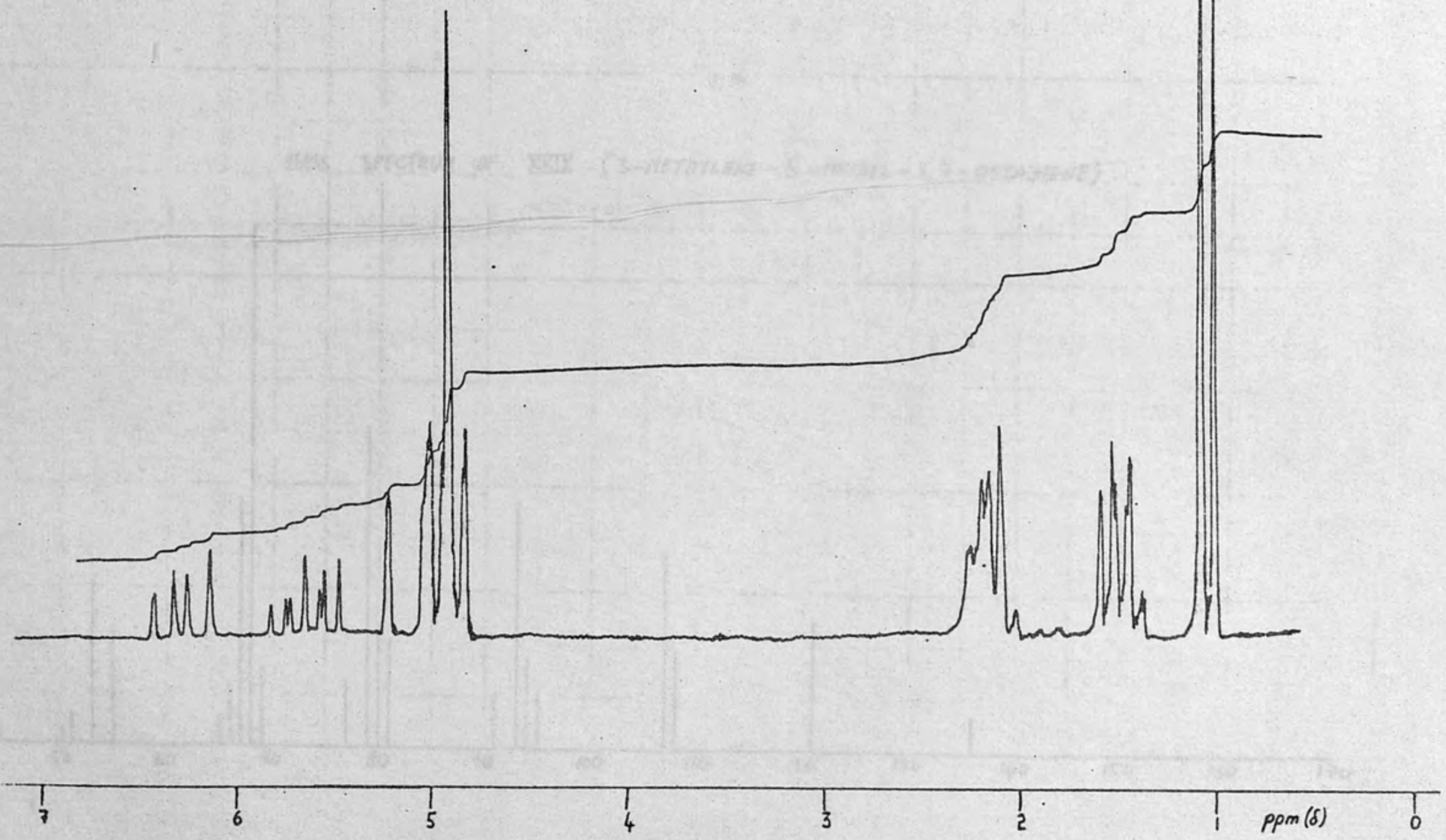
1595 cm^{-1} (medium) : conjugated double bounds

1640 cm^{-1} (medium) : isolated double bound

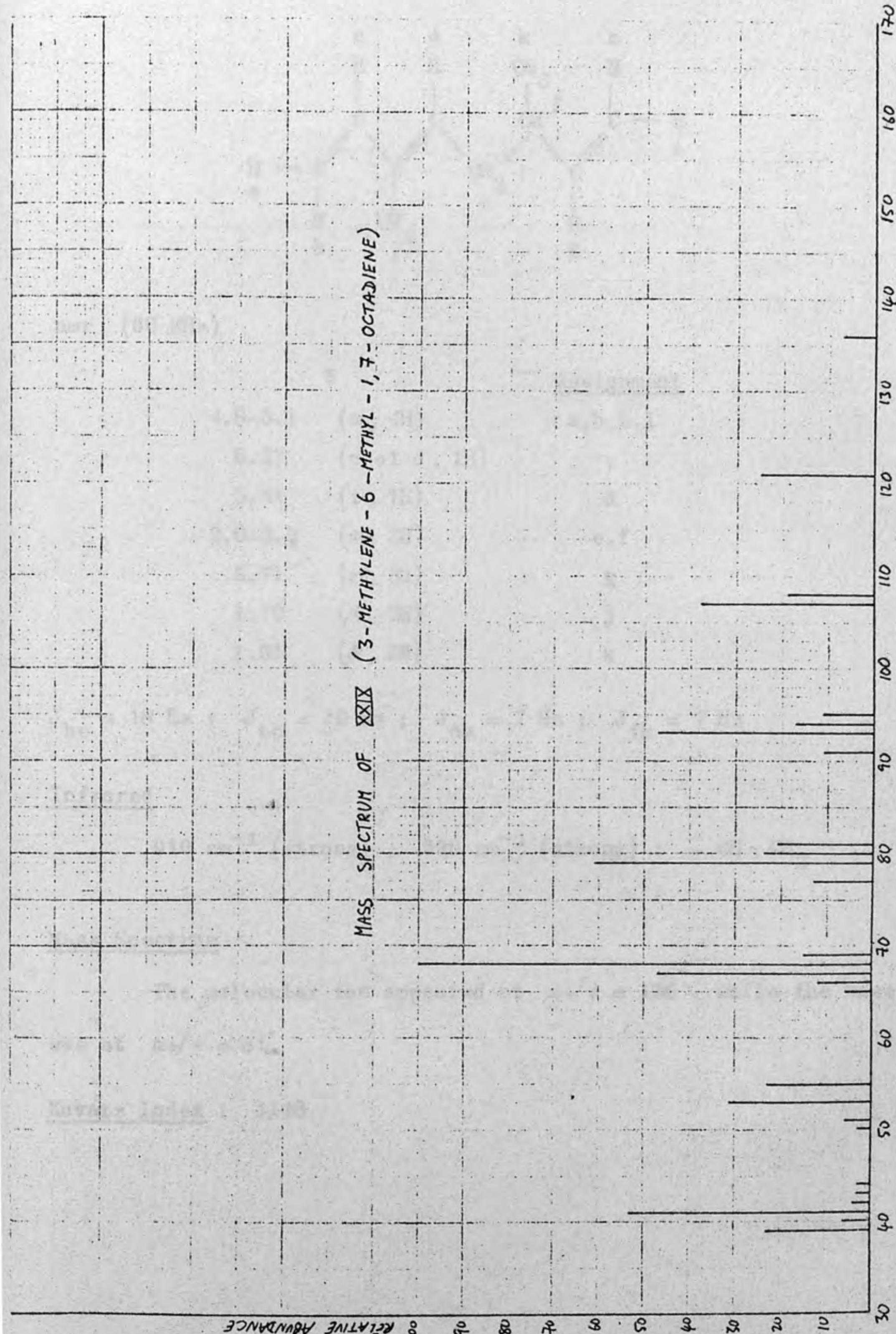
Mass Spectrum

The mass spectrum had the molecular ion at m+/e = ~~168~~ 136 as required for $C_{10}H_{16}$. The base peak occurred at m+/e = 68.

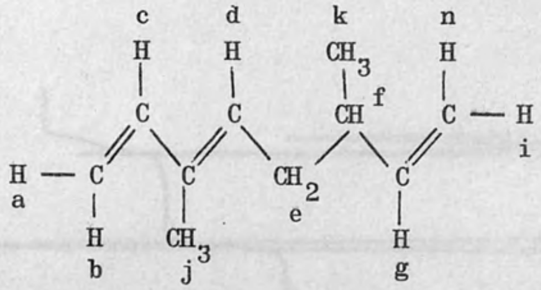
Kováts Index : 1099



100MHz nmr SPECTRUM OF XXIX


MASS SPECTRUM OF XXIX (3-METHYLENE - 6 -METHYL - 1,7 - OCTADIENE)
RELATIVE ABUNDANCE
100
90
80
70
60
50
40
30
20
10
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170

XXX 3,6-Dimethyl-1,trans-3,7-octatriene



nmr (60 MHz)

δ		Assignment
4.8-5.1	(m , 4H)	a,b,h,i
6.27	(d of d , 1H)	c
5.41	(t , 1H)	d
2.0-2.3	(m , 3H)	e,f
5.71	(m , 3H)	g
1.70	(s , 3H)	j
1.01	(d , 3H)	k

$J_{bc} = 18$ Hz ; $J_{ac} = 10$ Hz ; $J_{de} = 7$ Hz ; $J_{fk} = 7$ Hz

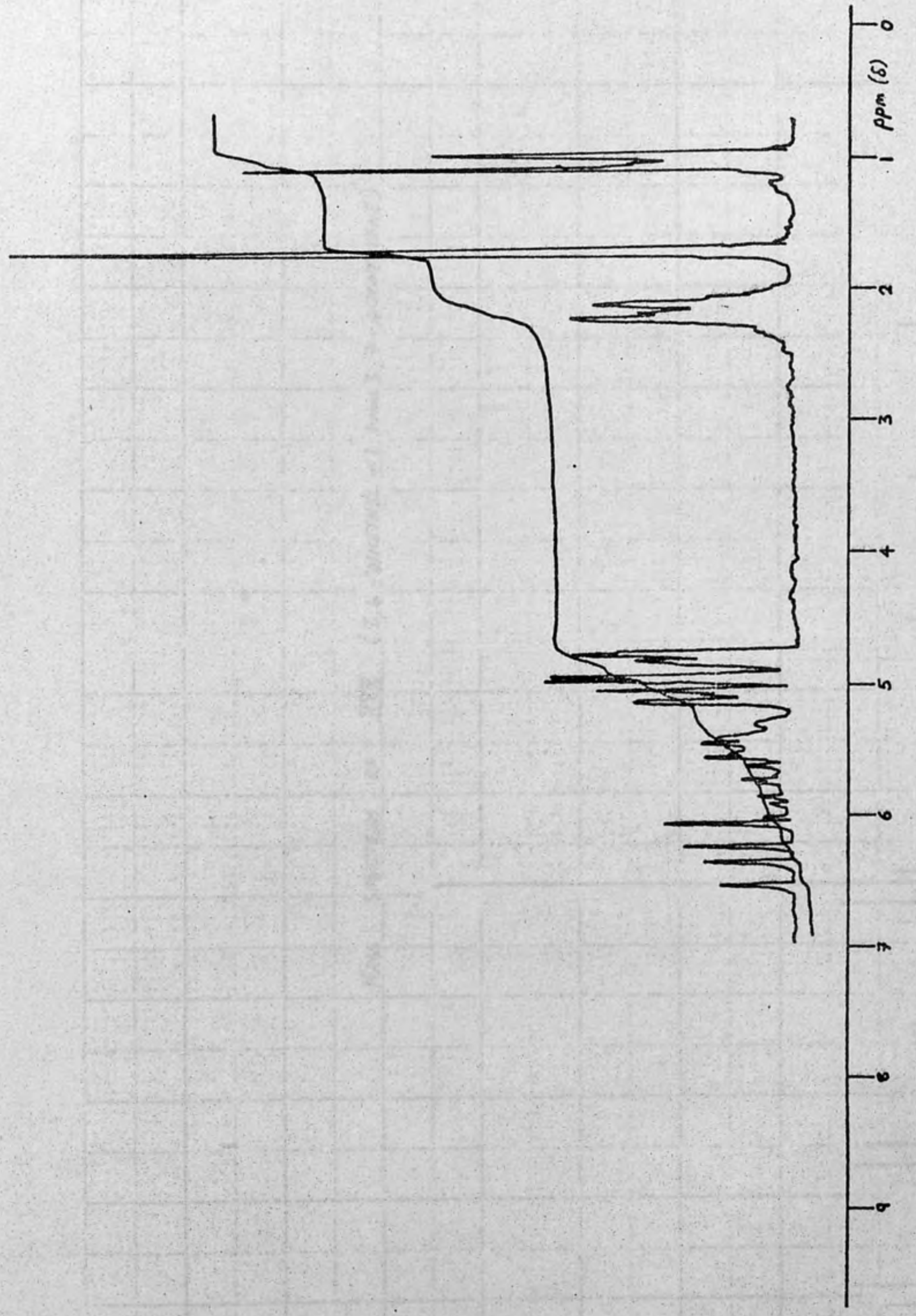
Infrared

910 cm^{-1} (strong) , 990 cm^{-1} (strong) : $- CH = CH_2$

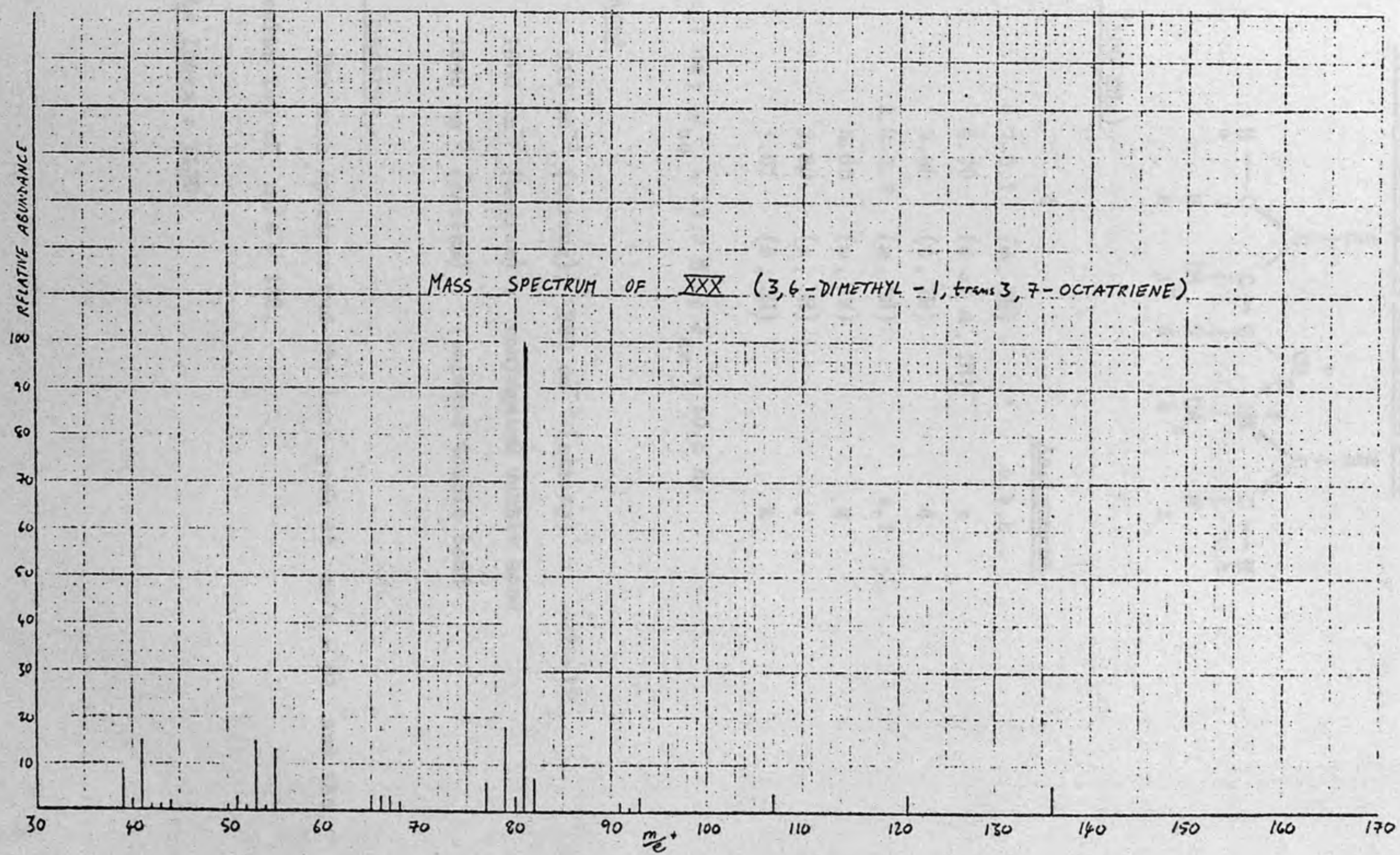
Mass Spectrum

The molecular ion appeared at m+/e = 136 , while the base peak was at m+/e = 81.

Kovàts Index : 1148

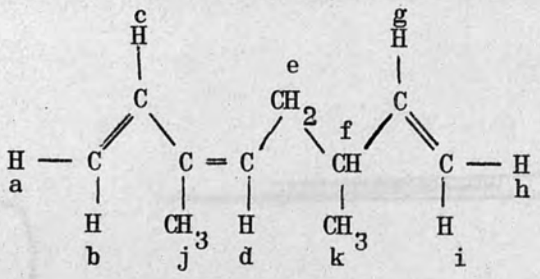


60 MHz ¹H nmr SPECTRUM OF XXX



MASS SPECTRUM OF XXX (3,6-DIMETHYL-1, trans 3, 7-OCTATRIENE)

XXXI 3,6-Dimethyl-1, cis-3,7-octatriene



nmr (100 MHz)

δ		Assignment
4.7-5.1	(m , 4H)	a,b,h,i
6.70	(d of d , 1H)	c
5.30	(t , 1H)	d
2.0-2.3	(m , 3H)	e,f
5.65	(m , 1H)	g
1.80	(s , 3H)	j
1.01	(d , 3H)	k

J_{fk} = 7 Hz ; J_{bc} = 17.5 Hz ; J_{ac} = 10.5 Hz

Infrared

910 cm^{-1} (strong), 990 cm^{-1} (strong) : $- CH = CH_2$

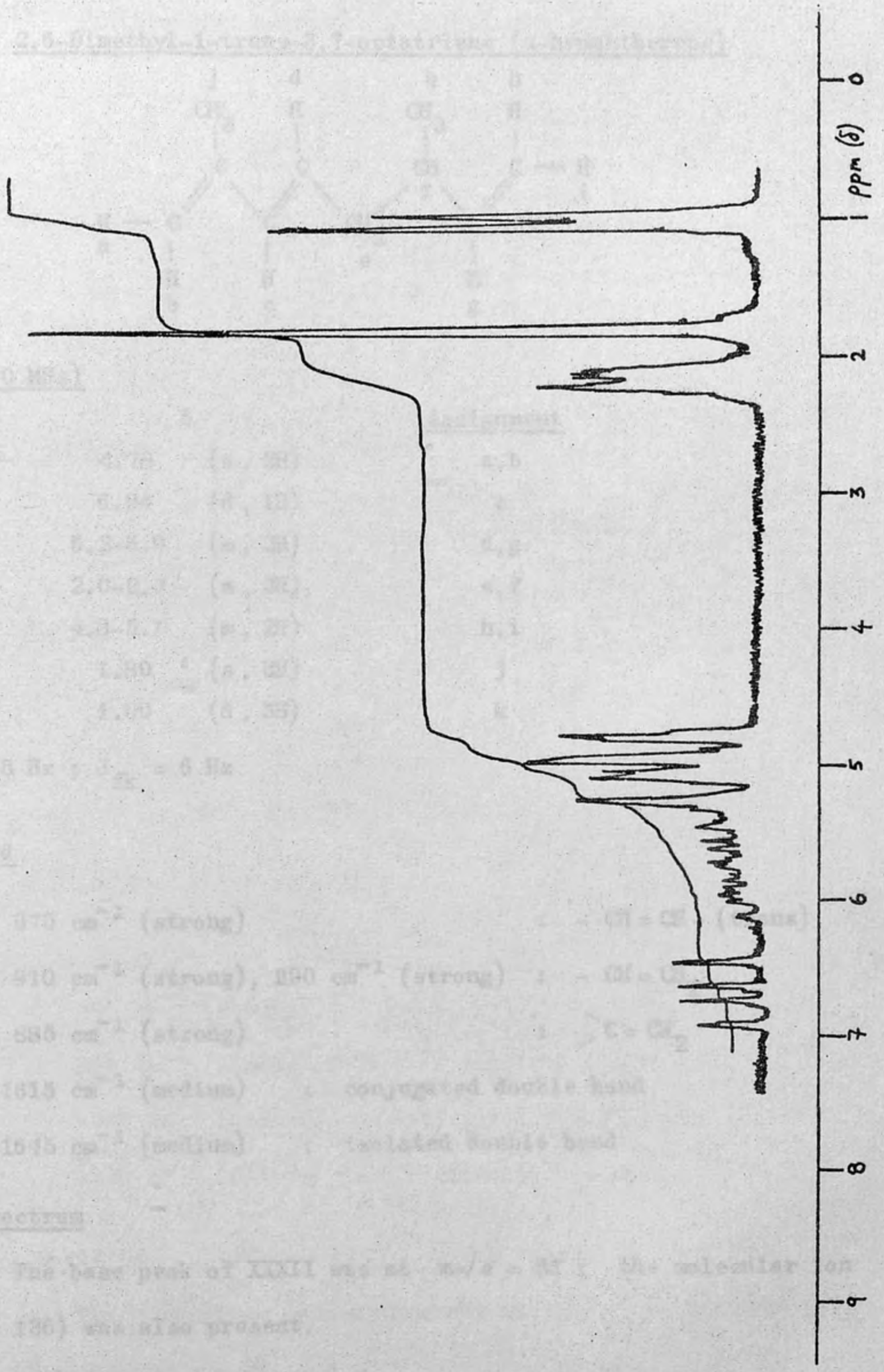
1600 cm^{-1} (medium) : conjugated double bond

1640 cm^{-1} (medium) : isolated double bond

Mass Spectrum

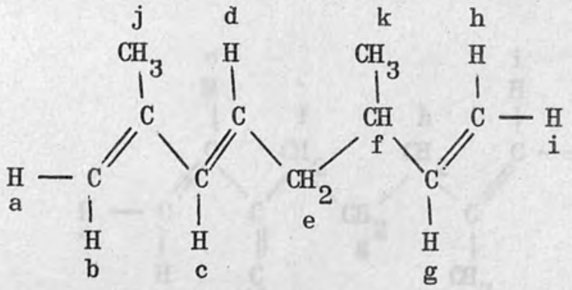
The mass spectrum had the base peak at m+/e = 81 and the molecular ion at m+/e = 136.

Kováts Index : 1130



60 MHz ¹H nmr SPECTRUM OF XXXI

XXXII 2,6-Dimethyl-1-trans-3,7-octatriene (α-hymentherene)



nmr (60 MHz)

δ		Assignment
4.78	(s , 2H)	a,b
6.04	(d , 1H)	c
5.2-5.9	(m , 2H)	d,g
2.0-2.3	(m , 3H)	e,f
4.8-5.1	(m , 2H)	h,i
1.80	(s , 3H)	j
1.00	(d , 3H)	k

$J_{cd} = 15$ Hz ; $J_{fk} = 6$ Hz

Infrared

970 cm^{-1} (strong) : $- CH = CH -$ (trans)

910 cm^{-1} (strong), 990 cm^{-1} (strong) : $- CH = CH_2$

885 cm^{-1} (strong) : $>C = CH_2$

1615 cm^{-1} (medium) : conjugated double bond

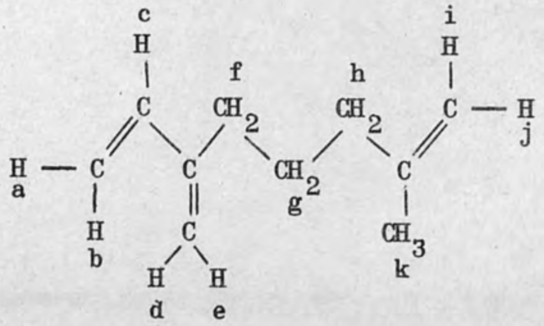
1645 cm^{-1} (medium) : isolated double bond

Mass Spectrum

The base peak of XXXII was at m+/e = 81 ; the molecular ion (m+/e = 136) was also present.

Kováts Index : 1126

XXXIII 3-Methylene-7-methyl-1,7-octadiene (α-myrcene)



nmr (100 MHz)

δ		Assignment
4.9-5.2	(m , 2H)	a,b
6.26	(d of d , 1H)	c
4.95	(s , 2H)	d,e
1.9-2.3	(m , 4H)	f,h
1.4-1.6	(m , 2H)	g
4.63	(s , 2H)	i,j
1.68	(s , 3H)	k

J_{bc} = 17.5 Hz ; J_{ac} = 10.5 Hz .

Infrared

895 cm^{-1} (strong) : $C = CH_2$

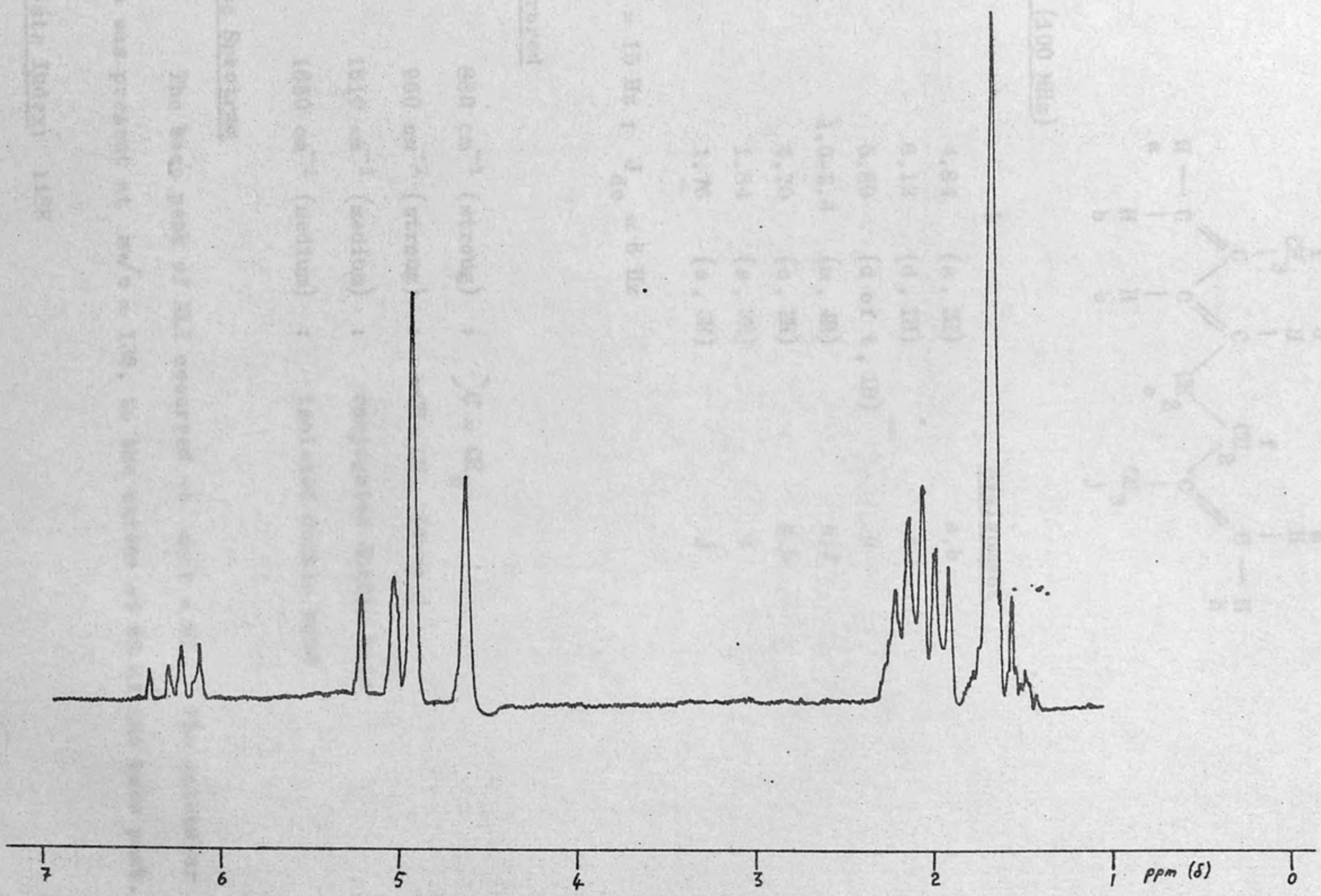
905 cm^{-1} (strong), 995 cm^{-1} (strong) : $-CH = CH_2$

1600 cm^{-1} (medium) : conjugated double bonds

1650 cm^{-1} (medium) : isolated double bond

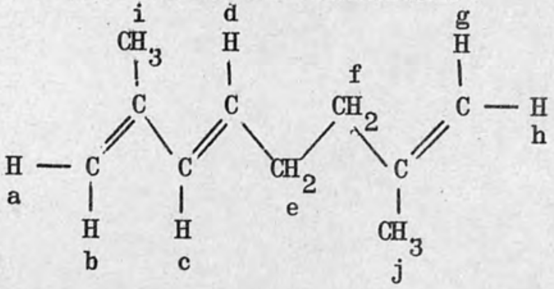
Mass Spectrum

The moleculare ion was present at m+/e = 136. The base peak occurred at m+/e = 68.



100MHz ^{1}H nmr SPECTRUM OF XXXIII

XLI 2,7-Dimethyl-1,trans-3,7-octatriene



nmr (100 MHz)

δ		Assignment
4.84	(s, 2H)	a,b
6.13	(d, 1H)	c
5.60	(d of t, 1H)	d
1.0-2.4	(m, 4H)	e,f
4.70	(s, 2H)	g,h
1.84	(s, 3H)	i
1.76	(s, 3H)	j

$J_{cd} = 15$ Hz ; $J_{de} = 6$ Hz

Infrared

880 cm^{-1} (strong) : $>C = CH_2$

960 cm^{-1} (strong) : $-CH = CH-$ (trans)

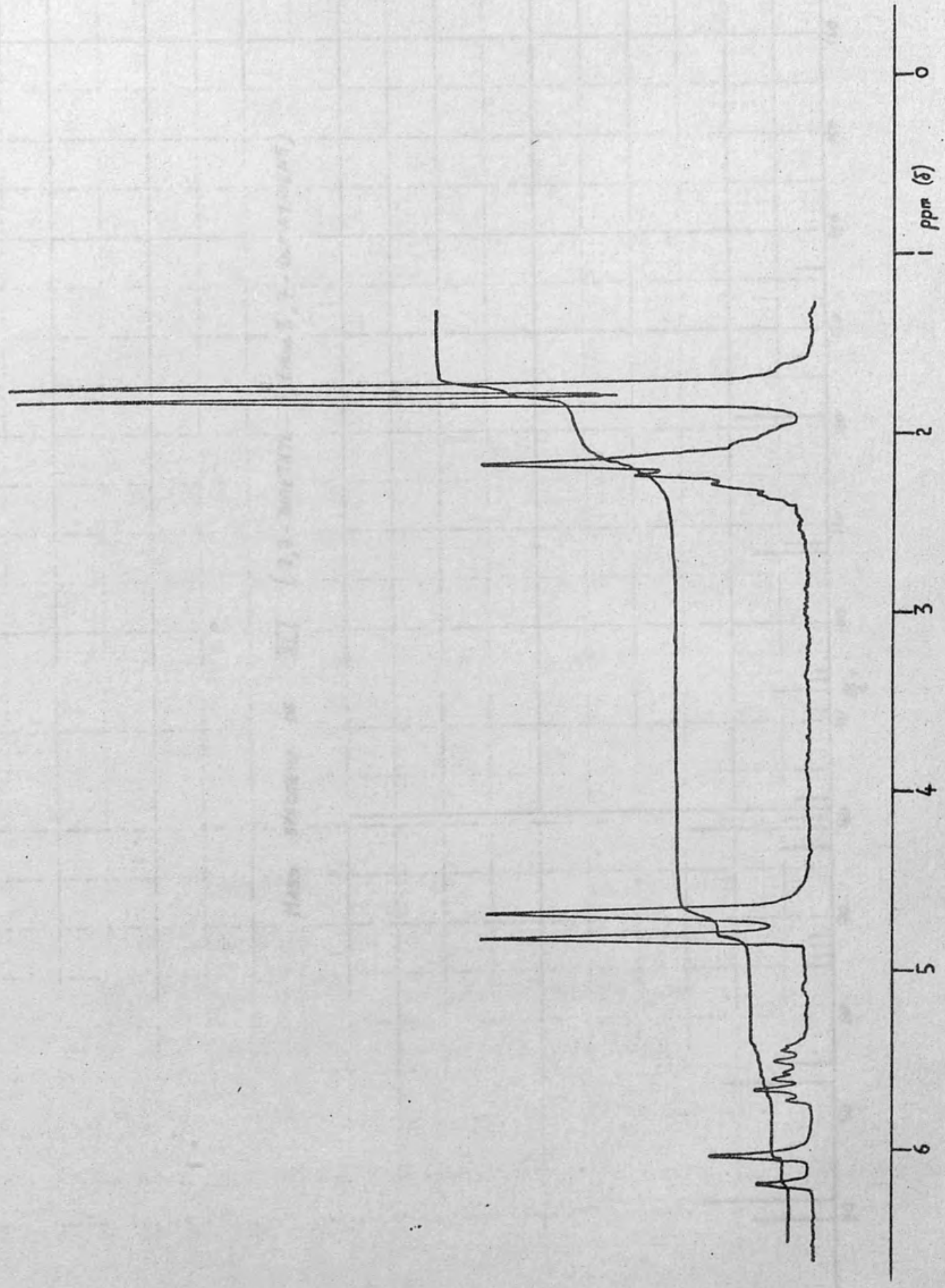
1610 cm^{-1} (medium) : conjugated double bond

1650 cm^{-1} (medium) : isolated double bond

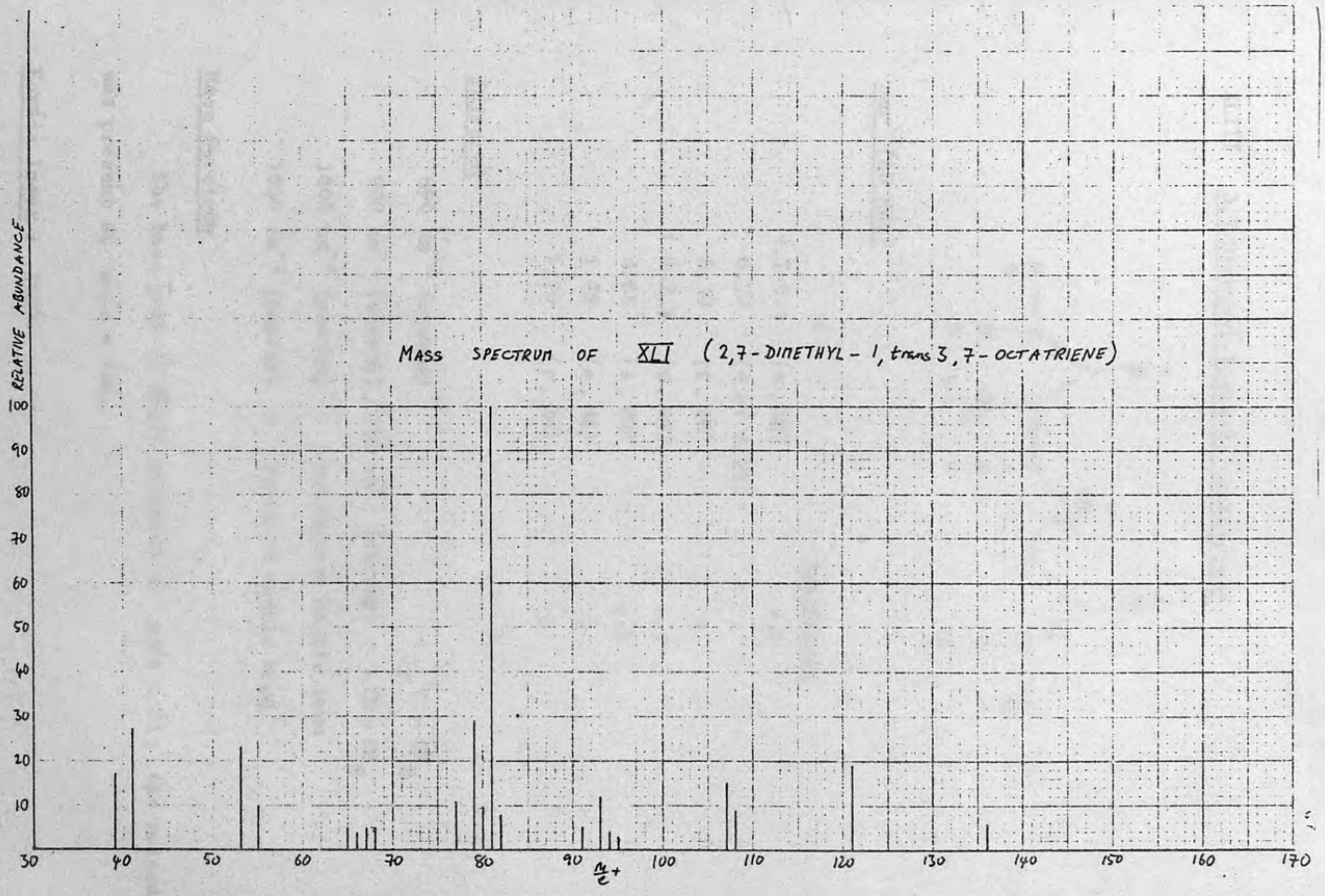
Mass Spectrum

The base peak of XLI occurred at m+/e = 81. The molecular ion was present at m+/e = 136, to the extent of 6% of the base peak.

Kováts Index: 1188

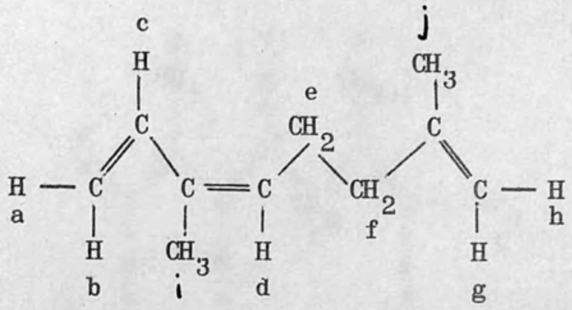


100MHz ^{1}H nmr SPECTRUM OF XLI



MASS SPECTRUM OF XLI (2,7-DIMETHYL-1, trans 3,7-OCTATRIENE)

XLIII 3,7-Dimethyl-1,cis-3,7-octatriene



nmr (60 MHz)

δ		Assignment
4.7-5.1	(m, 2H)	a,b
6.70	(d of d, 1H)	c
5.30	(t, 1H)	d
1.9-2.3	(m, 4H)	e,f
4.65	(s, 2H)	g,h
1.78	(s, 3H)	i
1.70	(s, 3H)	j

Infrared

890 cm^{-1} (strong) : $>C = CH_2$

900 cm^{-1} (strong), 990 cm^{-1} (strong) : $-CH=CH_2$

1605 cm^{-1} (medium) : conjugated double bond

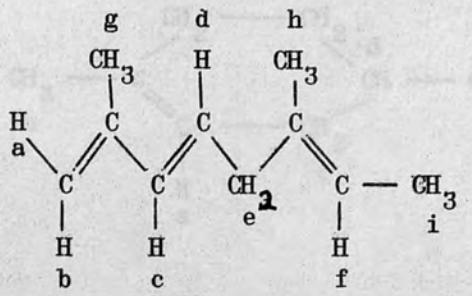
1650 cm^{-1} (medium) : isolated double bond

Mass Spectrum

The base peak of XLIII occurred at m+/e = 81; the molecular ion was present at m+/e = 136.

Kovàts Index : 1183

XLIV 2,6-Dimethyl-1,trans-3,trans-6-octatriene



nmr (100 MHz)

δ		Assignment
4.83	(s , 2H)	a,b
6.06	(d , 1H)	c
5.1-5.7	(m , 2H)	d,f
2.70	(d , 2H)	e
1.80	(s , 3H)	g
1.60	(broad singlet, 6H)	h,i

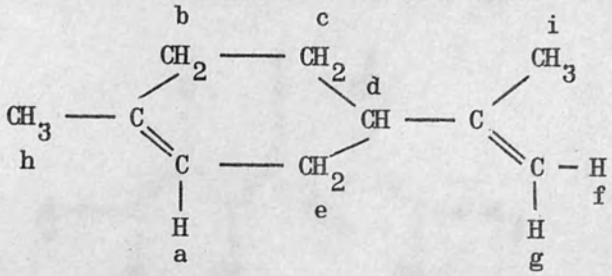
$J_{cd} = 15$ Hz .

Infrared

885 cm^{-1} (strong)	:	$\rangle C = CH_2$
970 cm^{-1} (strong)	:	$- CH = CH -$ (trans)
1610 cm^{-1} (medium)	:	conjugated double bond
1650 cm^{-1} (medium)	:	isolated double bond

Kováts Index : 1211

XLV **1-Methyl-4-isopropenyl-1-cyclo-hexene**



nmr

δ	Assignment
5.33 (broad singlet, 1H)	a
1.8-2.3 (m, 5H)	b, e, d
1.2-1.7 (m, 2H)	c
4.67 (s, 2H)	f,g
1.66 (s, 3H)	h
1.71 (s, 3H)	i

Infrared

890 cm^{-1} strong : $>C = CH_2$

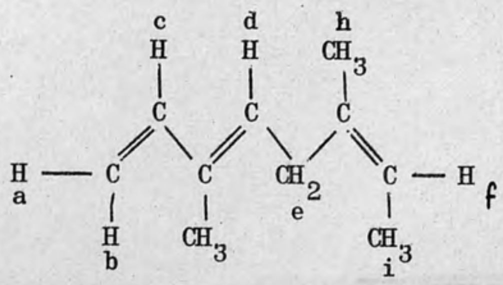
Mass Spectrum

The base peak in XLV occurred at m+/e = 68.

Kováts Index : 1201

The above spectral details, and the Kováts Index of XLV (1201) were identical with those of a sample of limonene supplied by Bush, Boake Allen Limited.

LI 3,6-Dimethyl-1,trans-3,~~trans~~cis-6-octatriene



nmr (100 MHz)

δ		Assignment
4.8-5.1	(m , 2H)	a,b
6.30	(d of d , 1H)	c
5.1-5.5	(m , 2H)	d,f
2.80	(d , 2H)	e
1.77	(s , 3H)	g
1.65	(s , 34)	h
1.60	(d , 3H)	i

$J_{bc} = 18$ Hz ; $J_{ac} = 10$ Hz ; $J_{de} = 9$ Hz.

Irradiation of proton d at δ5 , 29 partially collapsed the doublet due to protons e. Irradiation of proton f caused partial collapse of the doublet due to the methyl group i.

Infrared

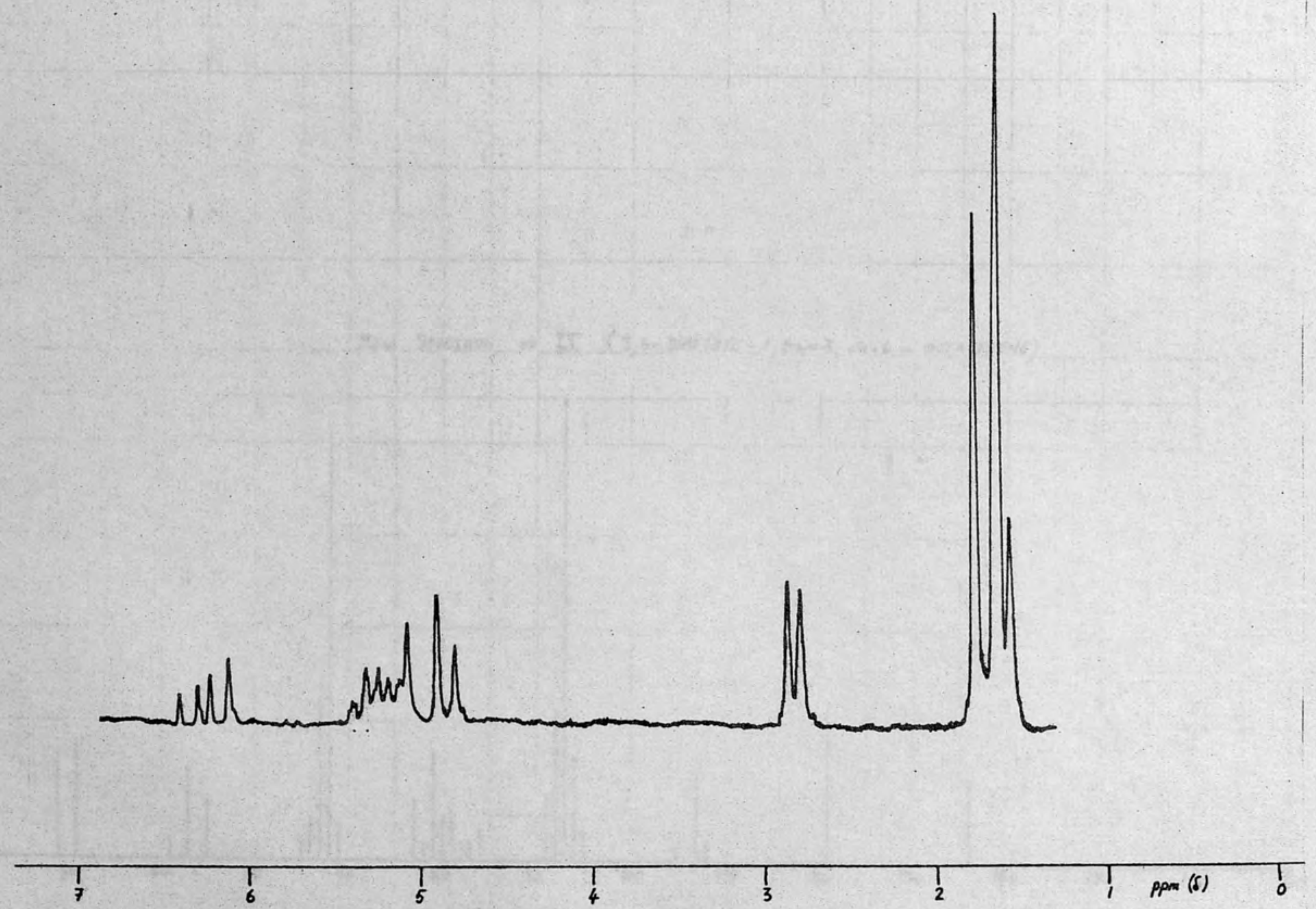
~~980 cm^{-1} (strong) : $>C=CH_2$~~

900 cm^{-1} (strong) , 995 cm^{-1} (strong) : $-CH=CH_2$

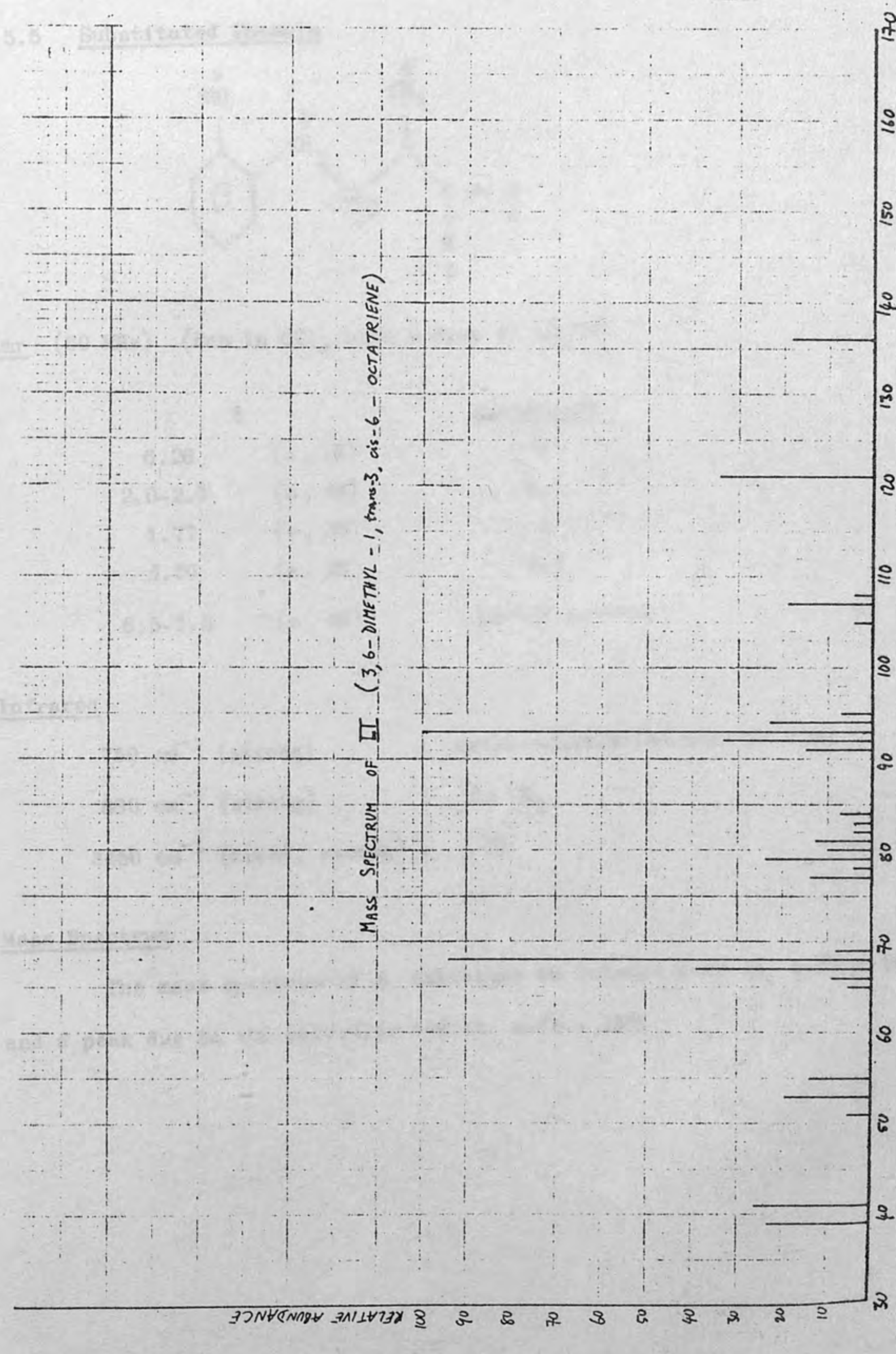
Mass Spectrum

Molecular ion : m+/e = 136

Base peak : m+/e = 93

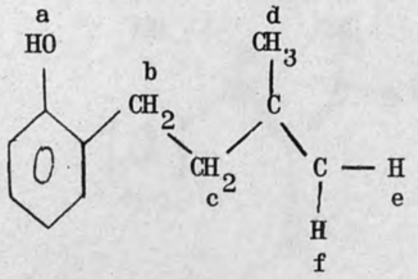


100 MHz ^{1}H nmr SPECTRUM OF LI



MASS SPECTRUM OF II (3,6-DIMETHYL-1, trans-3, cis-6 - OCTATRIENE)

6.5.5 Substituted Phenols



nmr (60 MHz) (Run in CCl_4 with a drop of CD_3CN)

δ		Assignment
6.26	(s , 1H)	a
2.0–2.9	(m , 4H)	b, c
1.77	(s , 3H)	d
4.70	(s , 2H)	e, f
6.5–7.2	(m , 4H)	phenyl protons

Infrared

750 cm^{-1} (strong) : ortho-substituted benzene ring

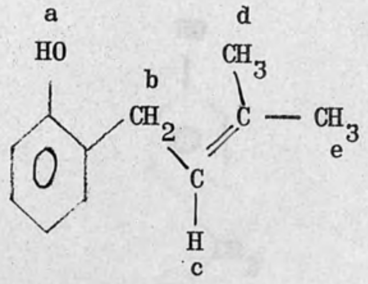
880 cm^{-1} (strong) : $>C=CH_2$

3450 cm^{-1} (broad, strong) : – OH

Mass Spectrum

The mass spectrum of L exhibited an intense peak at m+/e = 107, and a peak due to the molecular ion at m+/e = 162.

LII



nmr (60 MHz)

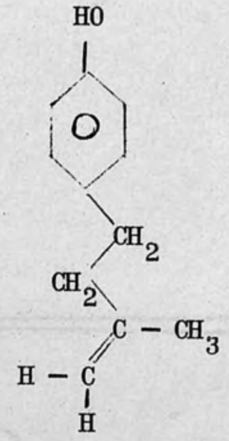
δ		Assignment
5.8	(s , 1H)	a
3.27	(d , 2H)	b
5.30	(t , 1H)	c
1.77	(s , 6H)	d, e
6.5–7.2	(m , 4H)	phenyl protons

Infrared

750 cm^{-1} (strong) : ortho-substituted benzene ring

3450 cm^{-1} (broad, strong) : – OH

LIII



nmr (60 MHz)

δ		Assignment
4.45	(s , 1H)	a
2.0-2.9	(m , 4H)	b, c
1.77	(s , 3H)	d
4.67	(s , 2H)	e, f
6.5-7.1	(q , 4H)	phenyl protons

Infrared

830 cm^{-1} (strong) : parasubstituted benzene ring

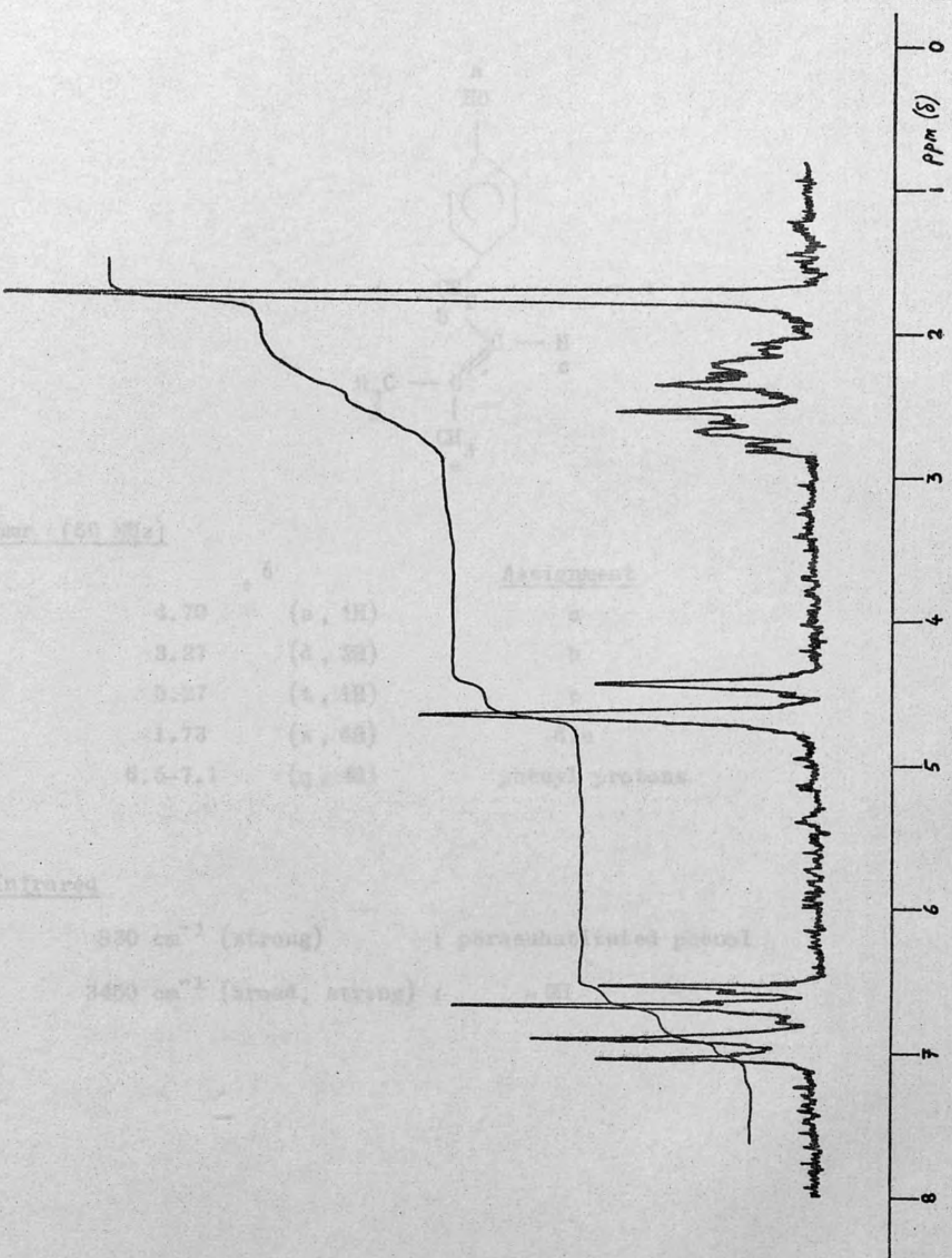
890 cm^{-1} (strong) : $>C = CH_2$

3450 cm^{-1} (broad, strong) : $-OH$

Mass Spectrometer

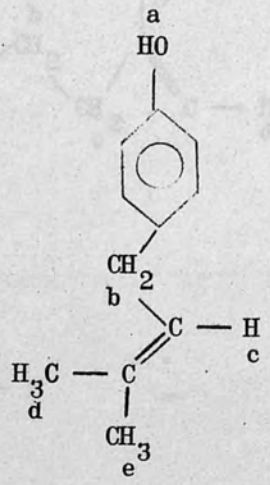
Molecular ion at m+/e = 162

Base peak at m+/e = 107 .



60MHz ^1H nmr SPECTRUM OF LIII

LIV



nmr (60 MHz)

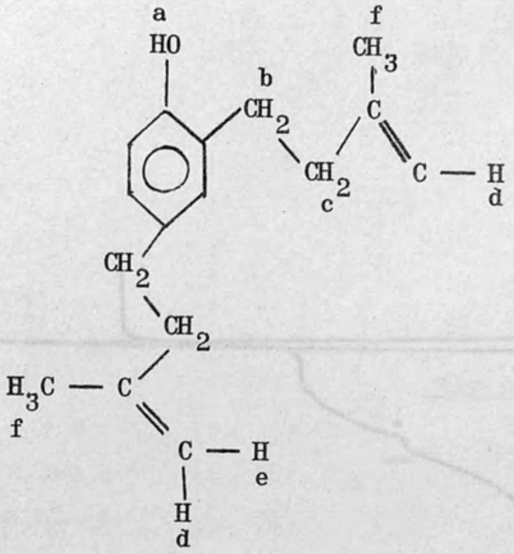
δ		Assignment
4.70	(s , 1H)	a
3.27	(d , 2H)	b
5.27	(t , 1H)	c
1.73	(s , 6H)	d, e
6.5–7.1	(q , 4H)	phenyl protons

Infrared

830 cm^{-1} (strong) : parasubstituted phenol

3450 cm^{-1} (broad, strong) : - OH

LV



nmr (60 MHz)

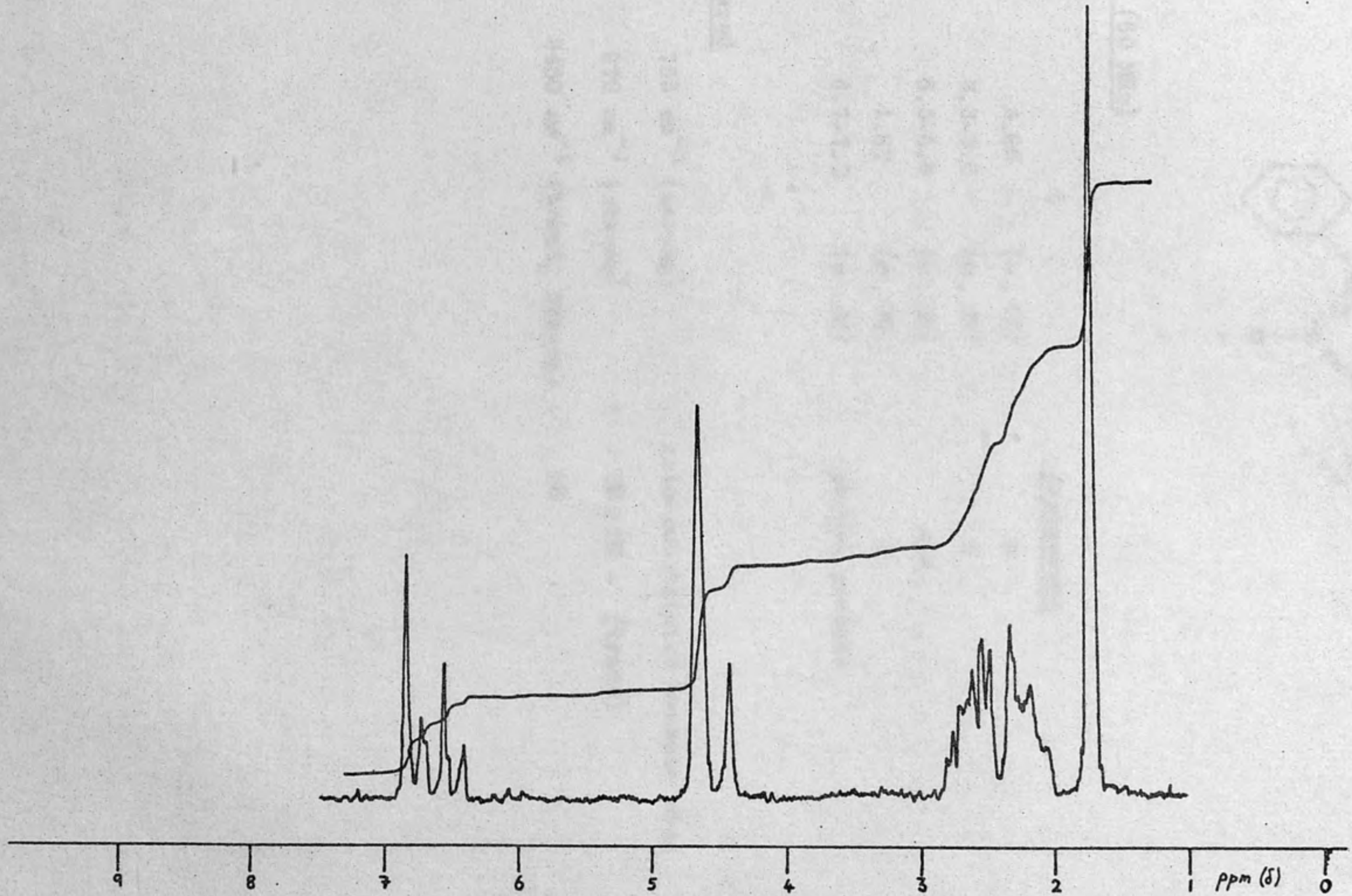
δ		Assignment
4.43	(s , 1H)	a
2.0-2.9	(m , 8H)	b, c
4.67	(s , 4H)	d, e
1.73	(s , 6H)	f
6.4-6.9	(m , 3H)	phenyl protons

Infrared

820 cm^{-1} (medium) : 1, 2, 4 - trisubstituted ring

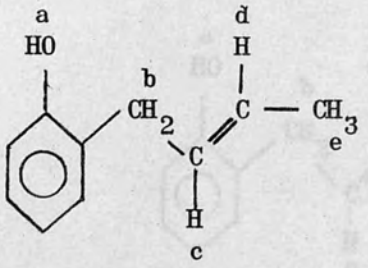
890 cm^{-1} (strong) : $>C=CH_2$

3500 cm^{-1} (broad, strong) : - OH



60 MHz ^{1}H nmr SPECTRUM OF LV

LVI



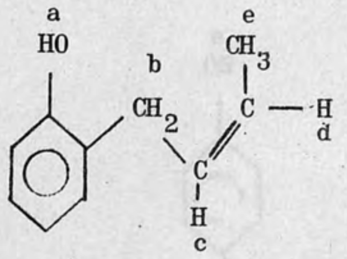
nmr (60 MHz)

δ		Assignment
4.86	(s , 1H)	a
3.3-3.6	(m , 2H)	b
6.5-6.9	(m , 2H)	c,d
1.87	(d , 3H	e
6.7-7.2	(m , 4H)	phenyl protons

Infrared

755 cm^{-1} (strong)	:	orthosubstituted benzene ring
970 cm^{-1} (strong)	:	- CH = CH - (trans)
3450 cm^{-1} (broad, strong)	:	- OH

LVII



nmr (60 MHz)

δ		Assignment
		a
3.33	(d , 2H)	b
5.2–6.1	(m , 2H)	c,d
1.75	(d , 3H)	c
6.5–7.2	(m , 4H)	phenyl protons

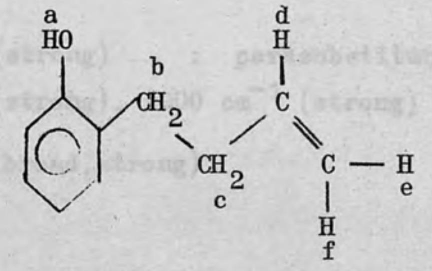
Infrared

695 cm^{-1} (medium) : - CH = CH - (cis)

755 cm^{-1} (strong) : orthosubstituted benzene ring

3450 cm^{-1} (broad, strong): - OH

LVIII



nmr

δ		Assignment
6.3	(s , 1H)	a
2.1–2.9	(m , 4H)	b, c
5.4–6.0	(m , 1H)	d
4.8–5.2	(m , 2H)	e, f
6.5–7.1	(m , 4H)	phenyl protons

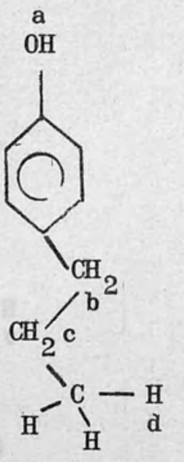
Infrared

755 cm^{-1} (strong) : orthosubstituted benzene ring

910 cm^{-1} (strong), 990 cm^{-1} (strong) : - CH = CH$_2$

3450 cm^{-1} (broad, strong) : - OH

LIX



nmr

δ		Assignment
4.8–5.2	(m , 3H)	a,e,f
1.0–2.9	(m , 4H)	b,c
5.4–6.2	(m , 1H)	d
6.5–7.2	(q , 4H)	phenyl protons

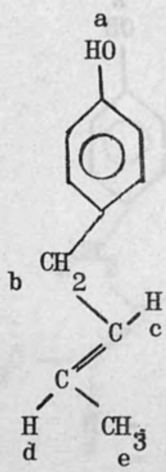
Infrared

830 cm^{-1} (strong) : parasubstituted benzene ring

915 cm^{-1} (strong), 1000 cm^{-1} (strong) : $-CH=CH_2$

3500 cm^{-1} (broad, strong) : $-OH$

LX



nmr (60 MHz)

δ		Assignment
4.70	(s , 1H)	a
3.25	(m , 2H)	b
5.1-5.8	(m , 2H)	c,d
1.73	(d , 3H)	e
6.5-7.1	(q , 4H)	phenyl protons

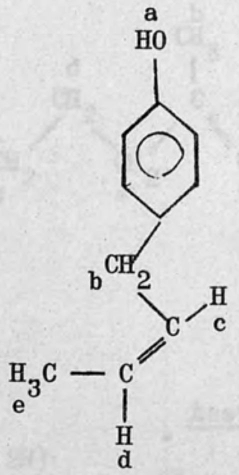
Infrared

830 cm^{-1} (strong) : para-substituted benzene ring

970 cm^{-1} (strong) : - CH = CH - (trans)

3400 cm^{-1} (broad, strong) : - OH

LXI



nmr (60 MHz)

δ		Assignment
4.55	(s , 1H)	a
3.2–3.4	(m , 2H)	b
5.3–5.8	(m , 2H)	c,d
1.72	(d , 3H)	e
6.5–7.1	(q , 4H)	phenyl protons

Infrared

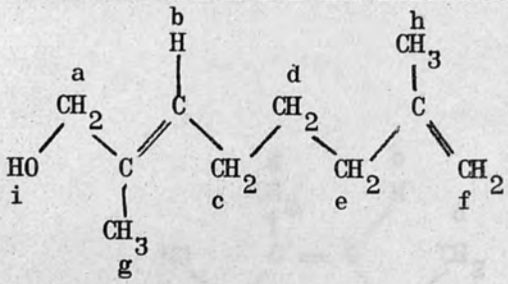
690 cm^{-1} (medium) : – CH = CH – (cis)

825 cm^{-1} (strong) : parasubstituted ring

3400 cm^{-1} (broad, strong) : – OH

(vi) Alcohols

LXVIII 1-hydroxy-2,7-dimethyl-trans 2,7-octadiene



nmr (60 MHz)

δ		Assignment
3.87	(s , 2H)	a
5.33	(t , 1H)	b
1.8-2.2	(m , 4H)	c, e
1.3-1.6	(m , 2H)	d
1.63	(s , 3H)	g
1.70	(s , 3H)	h

Infrared

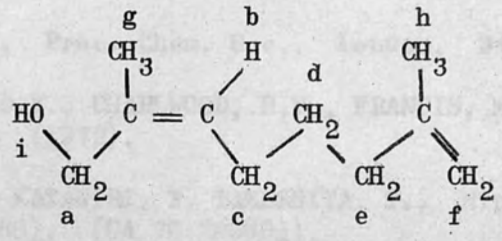
3400 cm^{-1} (broad, strong) : $-OH$

890 cm^{-1} (strong) : $>C=CH_2$

Mass Spectrum

Molecular ion : m+/e = 154 (correct for $C_{10}H_{18}O$)

LXIX 1-hydroxy-2,7-dimethyl - cis 2,7-octadiene



nmr 60 MHz

δ		Assignment
4.03	(s , 2H)	a
5.20	(t , 1H)	b
1.8-2.2	(m , 4H)	c,e
1.3-1.6	(m, 2H)	d
4.63	(s , 2H)	f
1.77	(s , 3H)	g
1.70	(s , 3H)	h

Infrared

3400 cm^{-1} (broad, strong) : - OH

890 cm^{-1} (strong) : $>C=CH_2$

Mass Spectrum

Molecular ion : m+/e = 154

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