Tetrahedron. Vol 28, pp 3705 to 3720 Pergamon Press 1972. Printed in Great Britain

ORGANIC SYNTHESES BY MEANS OF NOBLE METAL COMPOUNDS—XLVII[1]

REACTION OF BUTADIENE WITH ALDEHYDES AND KETONES CATALYZED BY PALLADIUM–PHOSPHINE COMPLEXES

K. OHNO, T. MITSUYASU and J. TSUJI

Basic Research Laboratories, Toray Industries Inc., Kamakura, Japan

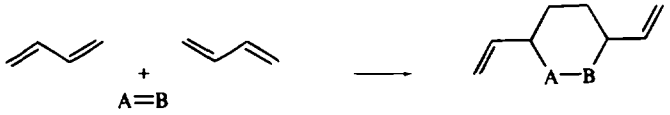
(*Received in Japan* 8 *January* 1972; *Received in the UK for publication* 19 *April* 1972)

Abstract— Palladium catalyzed reaction of butadiene with carbonyl compounds yields 1-substituted 2-vinyl-4, 6-heptadien —1-ols or 2-substituted 3,6-divinyltetrahydropyrans. Four stereoisomeric pyrans were characterized by NMR analysis. The reaction mechanism is discussed.

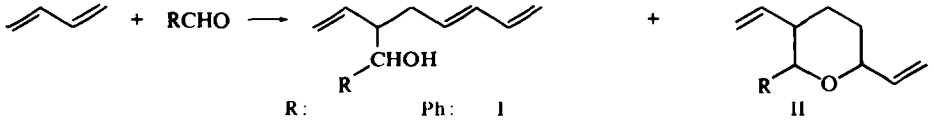
INTRODUCTION

PALLADIUM is an active catalyst for the decarbonylation of aldehydes.[2] From careful consideration of the reaction mechanism, we assumed the first step to be oxidative addition of aldehyde to the palladium catalyst to form an acyl-palladium complex,[3] which could be an active intermediate for olefin insertion.[4] In an attempt to synthesise ketones by olefin insertion into an acyl-palladium bond, we carried out the reaction of butadiene with aldehyde in the presence of a palladium–triphenylphosphine complex. Unexpectedly, the products obtained were not ketones but 1-substituted 2-vinyl-4,6-heptadien-1-ols and 2-substituted-3,6-divinyltetrahydropyrans. Preliminary accounts of this new reaction have been given from our laboratory,[5] and by others.[6,7]

This reaction seems to be a new general reaction of butadiene with a dipolar double bond to form cyclized products as expressed by the following scheme.



The reaction of isocyanates with butadiene to form divinylpiperidones provides another example of this general scheme.[8]

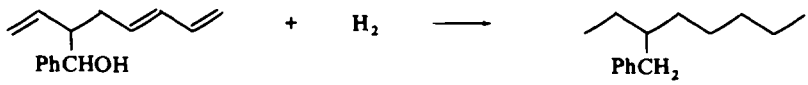


R:			
	Ph:	I	II
	p-ClC_6H_4:	III	IV
	p-MeC_6H_4:	V	VI
	p-$MeOC_6H_4$:	VII	VIII
	C_4H_3O:	IX	X
	Me:		XI
	Et:		XIII
	n-Pr:		XIV
	i-Pr:		XV

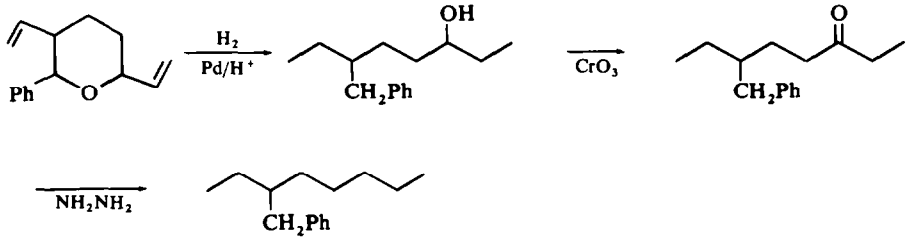
RESULTS AND DISCUSSION

Reaction with aromatic aldehydes

Benzaldehyde was treated with butadiene using a palladium–triphenylphosphine complex as catalyst, and the products separated into two components by fractional distillation. The high boiling fraction was found to be 1-phenyl-2-vinyl-4,6-heptadien-1-ol (I) by the following evidence. Elemental analysis and MW determination by mass spectrometry support formula $C_{15}H_{18}O$, derived from two moles of butadiene and one mole of benzaldehyde. The IR and NMR spectra also agree with the proposed structure. Hydrogenolytic hydrogenation over Pd/C consumed 4 moles of hydrogen to give 3-benzyloctane as below.



The low boiling fraction was determined to be 2-phenyl-3,6-divinyltetrahydropyran(II) by the following evidence. Elemental analysis and MW determination support formula $C_{15}H_{18}O$. It was converted into 6-benzyl-3-octanol by hydrogenation and hydrogenolytic ring opening at the benzylic ether bond. Oxidation of the alcohol with CrO_3 gave 6-benzyl-3-octanone which was converted into 3-benzyloctane by Wolff Kishner reduction.



Several types of palladium catalysts can be used for this reaction, most simply, palladium acetate or palladium acetylacetonate with triphenylphosphine. Also the π-allylpalladium chloride dimer, and dichlorobis(triphenylphosphine)palladium are active catalysts in the presence of excess base, e.g. NaOPh. Zero valent complexes such as tetrakis(triphenylphosphine)palladium, and bis(triphenylphosphine) palladium maleic anhydride are also active. As ligands, triarylphosphines are most conveniently used. Trialkylphosphines and trialkylarsines are less reactive. The reaction can be carried out using THF, benzene, DMF, or t-BuOH as solvent, even at room temperature (results are in Table I).

It was found that the ratio of products I and II can be controlled by changing the ratio of PPh_3/Pd in the catalytic species. I was obtained as main product when the ratio was near unity. By increasing the amount of PPh_3, the relative amount of II increased and II was formed nearly totally when the ratio was above two. This relationship is shown in Fig I using benzaldehyde.

The same pattern was repeated using several substituted benzaldehydes, the results are summarized in Table II.

TABLE I REACTION OF BENZALDEHYDE WITH BUTADIENE BY PALLADIUM CATALYSTS UNDER VARIOUS CONDITIONS

Catalyst (g)		NaOPh (g)	PhCHO (g)	Butadiene (ml)	Solvent (ml)	Temp (°C)	Time (hr)	I + II g(%)	II (%)	I (%)
$PdCl_2(PPh_3)_2$	(1·0)	1·0	16	40	none	80	3·5	15(47)	[f]	—
$PdCl_2(PPh_3)_2$	(0·45)	0·55	21	50	none	40–70	21	18 (43)	—	—
$PdCl_2(PPh_3)_2$	(0·5)	1·2	21	50	none	r.t.	68	28 (67)	92[g]	8
$PdCl_2(PPh_3)_2$	(0·2)	0·51	12	30	isopropanol (10)	r.t.	68	17·4 (72)	92·3[h]	7·7
$PdCl_2(PPh_3)_2$	(0·4)	0·82	21	50	isopropanol (50)	r.t.	68	21 (50)	—	—
$PdCl_2(PPh_3)_2$	(0·4)	0·88	21	50	THF (40)	72	17	25 (59)	82	18
$PdCl_2(PPh_3)_2$	(0·3)	0·7	11	25	MeCN (15)	70–88	16	9·4 (43)	73	27
$PdCl_2(DPE)$	(0·5)	0·63	21	50	none	80	6	31 (73)	86	14
$PdBr_2(DPE)_2$	(0·1)	0·5	21	50	none	80	20	trace	—	—
$Pd(PPh_3)_2(MA)$	(0·4)	0	22	50	none	70	44	24 (57)	97·2[i]	2·8
$PdCl_2(TPMP)_2$	(0·48)	0·6	21	35	none	80	5	22 (52)	91	9
$Pd(NO_2)_2(NH_3)_2$	(0·15)	0·67	22	50	benzene	23	88	1.3 (3)	—	..
$Pd(Py)_2Cl_2$	(0·12)	0·44	11	25	none	40	64	3·5 (16)	—	—
$Pd(DP)\cdot Cl_2$	(0·3)	0·8	21	50	benzene (20)	70	19	0·3 (0·7)	—	—
π-allyl $PdCl(PPh_3)$	(0·31)	1·1	21	50	none	r.t.	65	14·4 (34)	41[j]	59
π-allyl $PdCl(PPh_3)$ + PPh_3	(0·18) (0·57)	0·8	11	25	benzene (10)	70	17	18·4 (83)	96	4

DPE: tetraphenyldiphosphinoethane, MA: maleic anhydride, TPMP: tri(p-methoxyphenyl)phosphine, Py: Pyridine, DP: α,α'-dipyridil [f]II A/II B/II C = 38:48:14, [g]II A/II B/II C = 23:44:33, [h]II A/II B/II C = 27:45:28, [i]II A/II B/II C = 39:51:10, [j]II A/II B/II C = 43:32:25

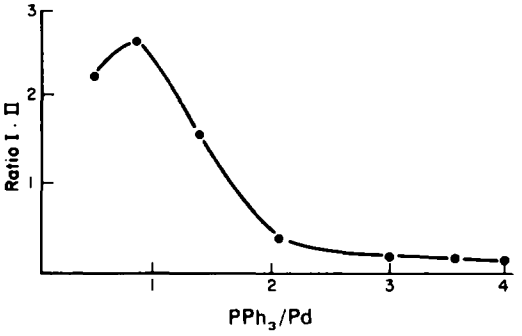
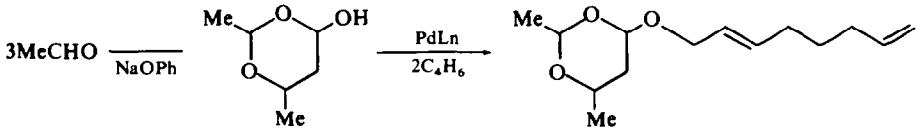


FIG I. The effect of PPh_3/Pd ratio on the reaction products.

Reaction with aliphatic aldehydes

The reaction with aliphatic aldehydes was carried out as shown in Table III. Since the reactions were carried out at the higher PPh_3/Pd ratio, pyrans were the main products and almost no alcohol was formed. But at the same time considerable amounts of other by-products were obtained. In the presence of dichlorobis(triphenylphosphine)palladium and NaOPh, 2-methyl-3,6-divinyltetrahydropyran (XI) was obtained from acetaldehyde accompanied by 2,4-dimethyl-6-(2,7-octadienyloxy)-1,3-dioxane(XII). Two stereoisomers of XI were separated by column chromatography and characterized. The formation of XII can be explained by base catalyzed trimerization of the aldehyde to give 6-hydroxy-2,4-dimethyl-1,3-dioxane,[9] followed by reaction of the resulting dioxane with butadiene. Thus, in the absence of the base, XII was not formed.



XII

n-Propionaldehyde, n-butyraldehyde, and isobutyraldehyde behaved similarly giving the corresponding divinylpyrans (XIII, XIV, and XV, respectively) in high yields.

Dichlorobis (triphenylphosphine) platinum with excess NaOPh can also be used for the reaction, though the activity was lower than that of palladium. In addition to the isopropyldivinylpyran (XV), a considerable amount of 2,6-diisopropyl-5,5-dimethyl-1,3-dioxan-4-on(XVI) was obtained from isobutyraldehyde. The formation of the latter can be explained by dehydrogenation of the aldehyde to give a ketene by the catalytic action of the platinum complex, followed by cyclization with isobutyraldehyde as shown below. The formation of butenes in this reaction was confirmed by GLPC analysis. The results are in Table V.

TABLE II. REACTION OF AROMATIC ALDEHYDES WITH BUTADIENE CATALYZED BY PALLADIUM COMPLEXES

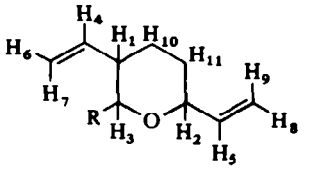
Aromatic aldehydes (g)	Catalyst (g)	NaOPh (g)	Butadiene (ml)	Solvent (ml)	Temp. (°C)	Time (hr)	Pyran + alcohol g(%) ratio[a]	B.p. (mm)
p-chlorobenzaldehyde (14)	$PdCl_2(PPh_3)$ (0·192)	0·827	30	benzene (30)	30	74	12·1 (49%) 9:91	120–138 (3)
p-methylbenzaldehyde (11)	$PdCl_2(PPh_3)$ (0·195)	0·537	20	benzene (10)	70–76	16	13 (62%) 12:88	115–140 (3)
p-methoxybenzaldehyde (13·6)	$Pd(OCOCH_3)_2$ (0·056) + PPh_3 (0·95)	—	20	isopropanol (30)	80	17	12·5 (51%) 11:89	120–140 (3)
furfural (20)	$PdCl_2(PPh_3)_2$	0·55	50	none	70	44	32·6 (76%)	85–105 (3)
furfural (28·8)	$Pd(OCOCH_3)_2$ (0·224) + PPh_3 (1·31)	—	80	isopropanol (70)	80	16	55 (90%)	

[a] Determined by GLPC analysis. (alcohol : Pyran).

TABLE III. REACTION OF ALIPHATIC ALDEHYDES WITH BUTADIENE CATALYZED BY PALLADIUM COMPLEXES

Aldehydes (g)	Catalyst (g)		NaPh (g)	Butadiene (ml or g)	Solvent (ml)	Temp. (°C)	Time (hr)	2-Alkyl-3, 6-divinylpyran g, (%)	B.p. (mm)
acetaldehyde (11)	$PdCl_2(PPh_3)_2$	(0·35)	1·0	60 g	benzene (30)	80	17	XI, 7·6 (10)	70 100 (40)
acetaldehyde (46)	$Pd(OCOCH_3)_2$	(0·224)	—	160 ml	isopropanol (70)	60–70	17	XI, 106 (70)	
	PPh_3	(1·31)							
propionaldehyde (16·2)	$Pd(OCOCH_3)_2$	(0·225)	—	55 ml	isopropanol (50)	80	17	XIII, 25·5 (55)	95–110 (28)
	PPh_3	(1·31)							
n-butyraldehyde (21·6)	$Pd(OCOCH_3)_2$	(0·224)	—	80 ml	isopropanol (50)	80	17	XIV, 33·3 (62)	110–115 (40)
	PPh_3	(1·31)							
n-butyraldehyde (10)	$Pd(PPh_3)_4$	(0·2)	—	30 ml	none	124–130	8	XIV, 5·8 (23)	
n-butyraldehyde (15)	$PdCl_2(PPh_3)_2$	(1·0)	1·0	35 ml	none	70	17	XIV, 14·3 (38)	
isobuyraldehyde (21·6)	$Pd(OCOCH_3)_2$	(0·336)	—	70 ml	t-BuOH (40)	80	17	XV, 15·4 (28·6)	95–110 (35)
	PPh_3	(1·18)			benzene (10)				
isobutyraldehyde (15)	$PdCl_2(PPh_3)_2$	(1·0)	0·5	35 ml	none	70	17	XV, 5·2 (14)	

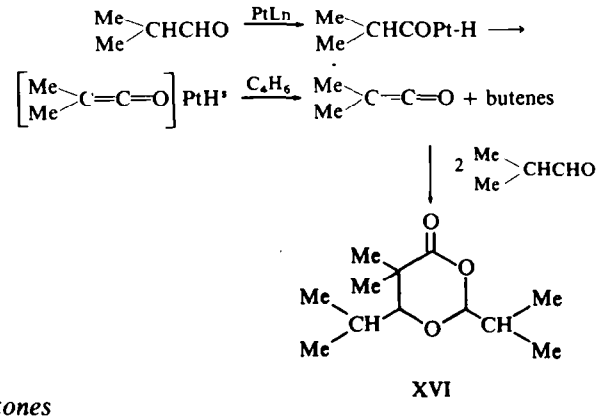
TABLE IV. NMR DATA OF ISOLATED 2-SUBSTITUTED-3,6-DIVINYLTETRAHYDROPYRAN (100 MHz, τ VALUE)



R (stereochemistry)[b]	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8	H_9	$H_{10} + H_{11}$	$J(H_2)$
Ph (II A; t(3), c(6))	7·84	6·12	6·05	4·56	4·16	5·22	5·26	5·01	4·81	8·95 ~ 8·6	$J_{1,3}(10)$, $J_{4,7}(16)$, $J_{4,6}(8)$, $J_{5,9}(16)$, $J_{5,8}(10)$
Ph (II B; c(3), c(6))	7·5	6·02	5·46	3·9 ~ 4·3		5·20	5·26	5·96	5·72	7·9 ~ 8·6	$J_{1,3}(2)$, $J_{4,7}(15)$, $J_{4,6}(8)$, $J_{5,9}(16)$, $J_{5,8}(10)$
Ph (II C; c(3), t(6))	7·48	5·48	5·19	3·86 ~ 4·26		5·16	5·21	4·81	4·82	7·9 ~ 8·5	$J_{1,3}(3)$, $J_{4,7}(18)$, $J_{4,6}(8)$, $J_{5,9}(16)$, $J_{5,8}(10)$
C_4H_3O (X A; c(3), e(6))	7·38	6·04	5·43	3·8 ~ 4·32			4·66 ~ 5·12			7·9 ~ 8·6	$J_{1,3}(2)$
C_4H_3O (X C; t(3), c(6))	7·49	6·17	5·95	4·05 ~ 4·7			4·75 ~ 5·2			7·8 ~ 8·7	$J_{1,3}(10)$, $J_{2,5}(3·6)$, $J_{2,10aq}(10)$, $J_{2,10eq}(2·4)$
Me (XI C; t(3), t(6))	a	5·67	6·55	3·96 ~ 4·60			4·78 ~ 5·13			8·0 ~ 8·6	$J_{1,3}(8)$, $J_{3,CH_3}(6)$, $J_{2,10eq}(3)$, $J_{2,10aq}(3)$
Me (XI D; c(3), t(6))	7·64	5·92	5·98	4·06 ~ 4·43			4·8 ~ 5·1			8·15 ~ 8·7	$J_{3,CH_3}(6·2)$, $J_{1,3}(4)$
iso-Pr (XV A; t(3), c(6))	7·84	6·24	6·98	3·95 ~ 4·6			4·65 ~ 5·1			8·0 ~ 8·7	$J_{3,isopropyl}(2)$, $J_{1,3}(10)$
iso-Pr (XV B; c(3), c(6))	7·60	6·24	7·08	3·6 ~ 4·25			4·65 ~ 5·0			8·1 ~ 8·6	$J_{3,isopropyl}(9)$, $J_{1,3}(2)$, $J_{1,4}(9)$
iso-Pr (XV D; c(3), t(6))	7·68	5·50	6·83	3·55 ~ 4·5			4·6 ~ 5·1			7·9 ~ 8·6	$J_{3,isopropyl}(10)$, $J_{1,3}(2)$

[a] Overlapped with the peak $H_{10} + H_{11}$.

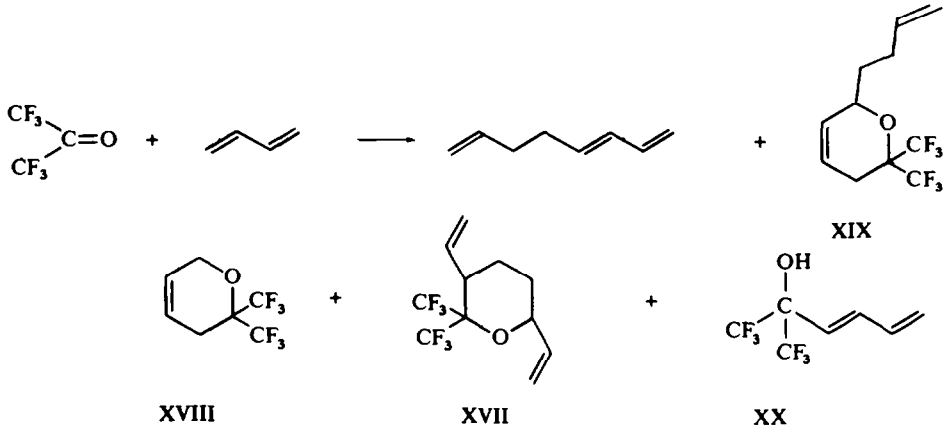
[b] t(3): *trans*-3, t(6): *trans*-6, c(3): *cis*-3, c(6): *cis*-6.



XVI

Reaction with ketones

The above palladium catalyzed reactions of butadiene proceed smoothly with most aldehydes, but reactions with simple ketones such as acetone were not successful and 1,3,7-octatriene was obtained.* However, some specific ketones were found to



XIX

XVIII XVII XX

TABLE V. REACTION OF ISOBUTYRALDEHYDE WITH BUTADIENE CATALYZED BY PLATINUM COMPLEXES

Catalysts (g)	Butadiene (ml)	Isobutyraldehyde (g)	Recovered Isobutyraldehyde[b] (g)	XV[b] (g)	XVI[b] (g)
$PtCl_2(PPh_3)_2$ (0·5) + PhONa (0·5)	35	15	7	3·5	4·5
$PtCl_2(PPh_3)_2$ (0·5) + PhONa (0·5)	—	15	12	—	—
$Pt(PPh_3)_4$ (0·38)	35	15	10	0·4	0·6
$PtCl_2(PPh_3)_2$ (0·5) + PhONa (0·5)	20 kg/cm[a]	15	7	—	—

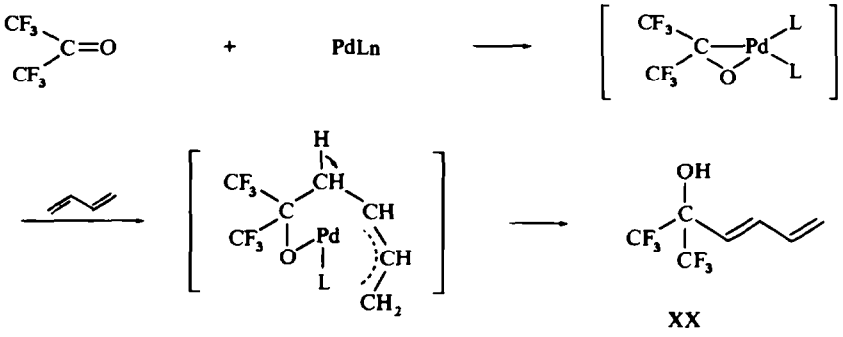
[a] Ethylene was used instead of butadiene.

[b] Obtained by distillation.

* The formation of 1,3,7-octatriene in acetone using bis(triphenylphosphine) palladium maleic anhydride as catalyst was reported (ref. 10).

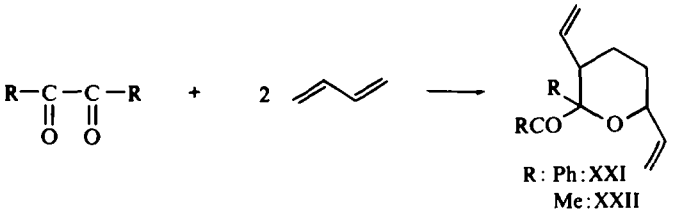
take part in the reaction. Thus, perfluoroacetone gave 2,2-bis (trifluoromethyl)-3,6-divinyltetrahydropyran (XVII), in addition to other products as shown below.

Both XVII and XIX were formed by Diels–Alder reactions of perfluoroacetone with butadiene and 1,3,7-octatriene.[11] Alcohol XX is formed by reaction of butadiene with perfluoroacetone (1:1), probably by the following mechanism.*



XX

Other active α-diketones such as benzil and biacetyl gave the corresponding pyrans (XXI and XXII) by reaction at one of the carbonyl centres.

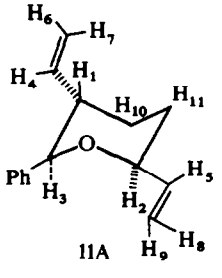


R: Ph:XXI
Me:XXII

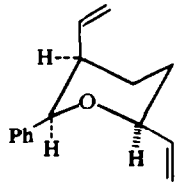
Stereochemistry of 2-substituted 3,6-divinyltetrahydropyrans

The obtained 2-substituted 3,6-divinyltetrahydropyrans consisted of four stereoisomers, some of which were separated by repeated column chromatography and are listed with their NMR data in Table IV.

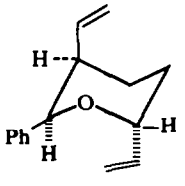
GLPC analysis of the 2-phenyl-3,6-divinyltetrahydropyrans showed three peaks: A(II A), B(II B), and C(II C)†. The peak of the fourth isomer overlapped with peak B. The NMR spectra of these three isomers are shown in Figs 2, 3, and 4.



11A



11B



11C

* Similar reaction was observed by Wilke *et al*[12] using a Nickel complex as stoichiometric reagent.

† Notation does not always reflect the same stereochemistry but the order of retension time on GLPC.

In the NMR spectrum of II B, when the H_5 proton was irradiated, the H_2 proton collapsed to a quartet. This means that the rate of inversion of the pyran ring is slow on the NMR time scale.[13] Otherwise, the quartet would collapse to a triplet by rapid inversion. The same observation was noted for II A and II C. Therefore, it seems logical that the large 2-phenyl moieties always prefer an equatorial conformation.

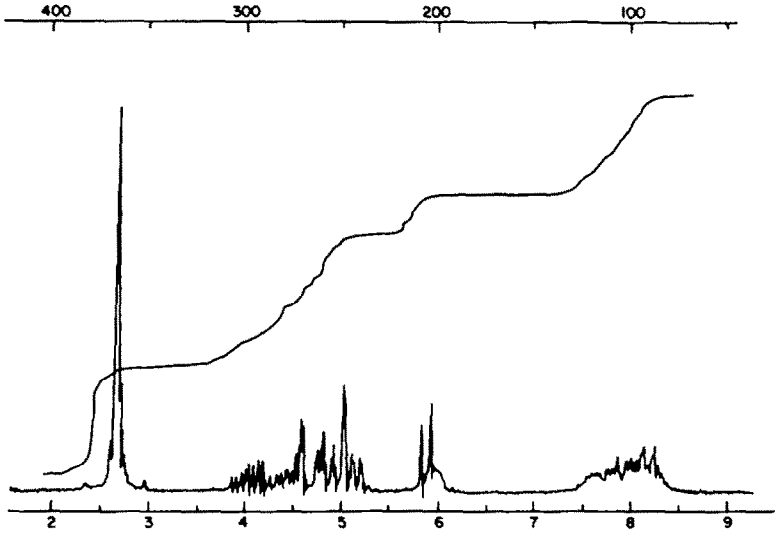


FIG 2. NMR spectrum of 2-phenyl-*trans*-3, *cis*-6-divinyltetrahydropyran (II A) (100 MHz, CCl_4).

The coupling constants $J_{1,3}$ of II A(10 Hz), II B(2 Hz) and II C(3 Hz) indicate their configuration as *trans*, *cis* and *cis* respectively. The H_2 signals are more complex and even decoupling experiments did not afford simple first-order spectra. The H_2 proton of II B is observed at higher field (6·02 τ) than that of II C.† Furthermore, the line width of the H_2 proton of II B (20 Hz) is larger than that of II C (10 Hz).‡

Thus, the H_2 protons of II B and II C should be axial and equatorial, respectively. Similarly the conformation of the 6-vinyl moiety of II A was deduced to be equatorial from the line width of the H_2 proton (20 Hz). From these data, compounds, II A, II B and II C were identified as 2-phenyl-*trans*-3, *cis*-6-divinyltetrahydropyran, 2-phenyl-*cis*-3, *cis*-6-divinyltetrahydropyran, and 2-phenyl-*cis*-3, *trans*-6-divinyltetrahydropyran, respectively.

GLPC analysis of 2-isopropyl-3,6-divinyltetrahydropyran also shows four peaks A, B, C and D in order of increasing retention time, three of which yielded pure material. The coupling constants $J_{1,3}$ of XV A, XV B, and XV D are 10 Hz, 2 Hz, and 2 Hz, respectively, which correspond to axial–axial, axial–equatorial, and axial–equatorial coupling. The chemical shifts of the H_2 protons of XV A, XV B,

† Usually the equatorial proton can be observed at lower field.[14]

‡ Broader line width seems to reflect axial–axial coupling.

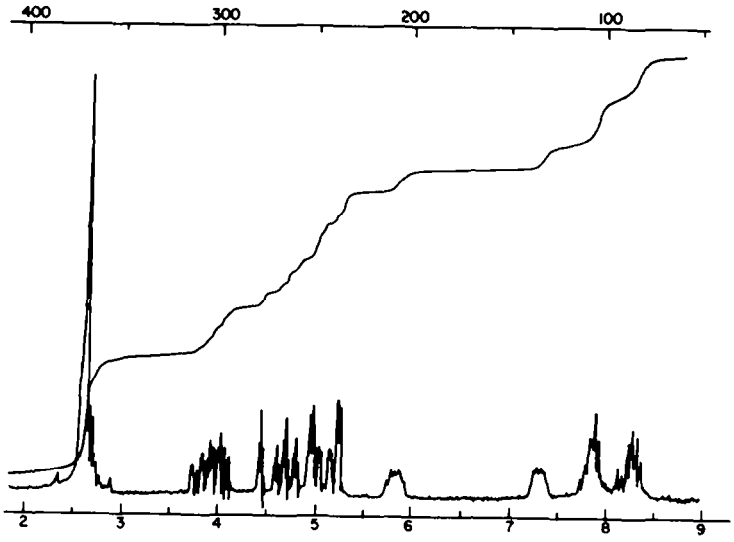


FIG 3. NMR spectrum of 2-phenyl-*cis*-3, *cis*-6-divinyltetrahydropyran (II B) (100 MHz, CCl_4).

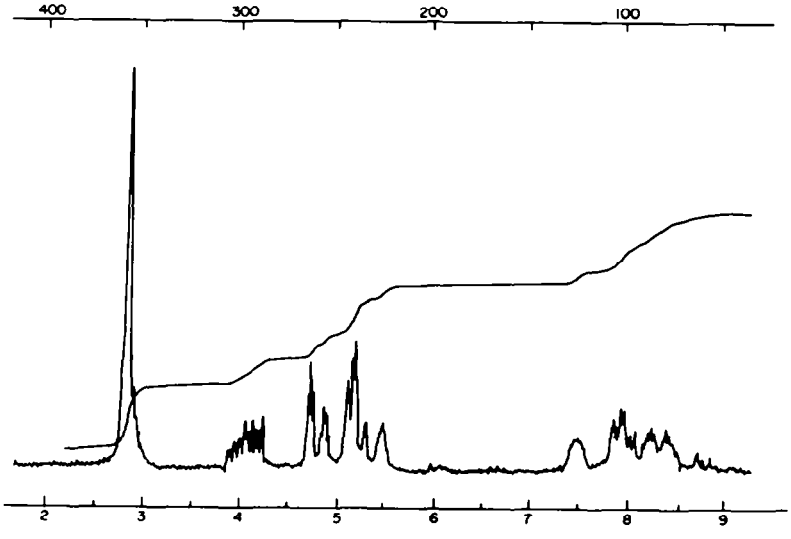


FIG 4. NMR spectrum of 2-phenyl-*cis*-3, *trans*-6-divinyltetrahydropyran (II C) (100 MHz, CCl_4).

and XV D are 6·24, 6·24, and 5·50 τ, respectively (Table IV). In the last case the H_2 proton is observed at lower field than those of the former two cases, and this proton would be equatorial. The line width of the H_2 protons (XV A, XV B, and XV D) are 20, 20, and 14 Hz, respectively. This suggests that the preferred conformations for the H_2 protons of XV A and XV B are axial and that of XV D equatorial. Their stereochemical assignments in Table IV follow from these data. The stereochemical assignments of other pyrans were made by similar techniques.

In the case of the 2-alkyl-3,6-divinyltetrahydropyrans (2-Me, 2-Et, 2-Pr, and 2-i-Pr derivatives), the gas chromatographic behavior of the four stereoisomers is relatively similar so that it seems probable that the peaks A, B, C, and D would have the *trans*-3, *cis*-6; *cis*-3, *cis*-6; *trans*-3, *trans*-6, and *cis*-3, *trans*-6 configurations, respectively, even though some were not isolated in a pure state.

The reaction mechanism

In 1968, N. Hagihara *et al.*[15] speculated that a σ,π-diallyl palladium complex, coordinated by phosphine, may be an intermediate in the butadiene. dimerization. They suggested that this intermediate might be protonated *via* σ-allyl palladium bond fission by a suitable protic medium followed by decomposition of the resulting mono-π-allyl palladium complex to yield the corresponding telomerization products.

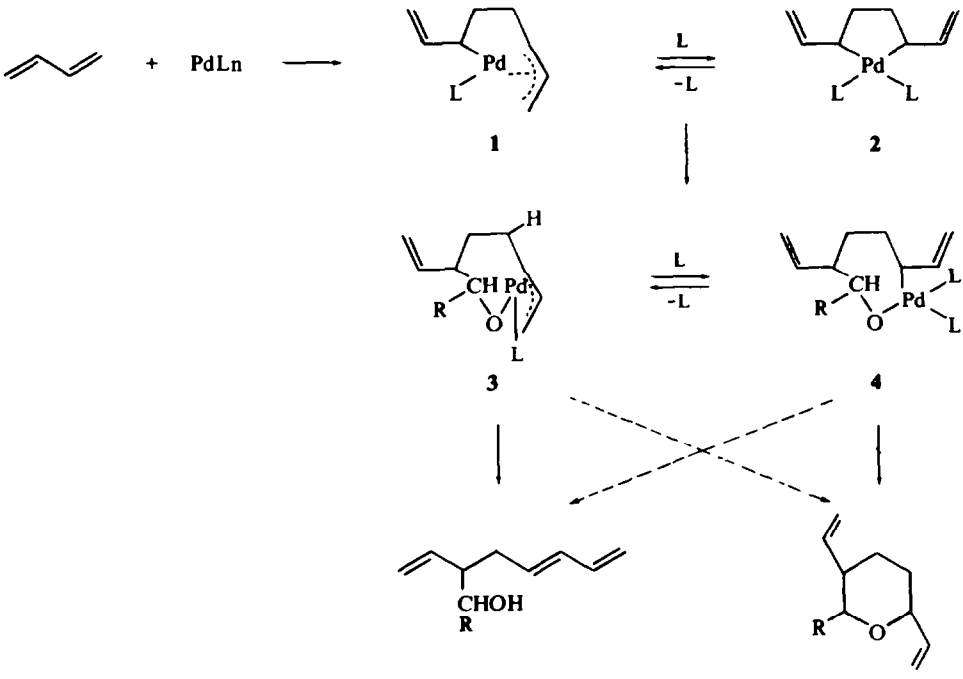
The same σ,π-diallyl palladium intermediates might play an important role in our novel reactions. In the presence of aldehydes, insertion of the carbonyl group into the palladium might take place giving an alkoxide type complex (3 or 4) as shown below. This intermediate would have an equilibrium between a π-allyl and σ-allyl palladium complex depending on the concentration of the phosphine ligands. The former complex is expected to decompose rapidly through hydrogen transfer from the α-position of the π-allyl moiety to give the unsaturated alcohol, while the latter complex might give rise to the pyran through a ligand coupling reaction. Generally, the alkoxide group of such a complex is transferred to the less substituted position of the π-allyl system through ligand coupling.* However, if the alkoxide group and π-allyl system are in the same molecule, this could not be general enough because of the geometrical restriction of the ligand. Thus, in the case of the pyran formation, the alkoxide group was certainly transferred to the more substituted site.

The presence of this equilibrium between the π-allyl and σ-allyl palladium complex was supported by experimental results (Fig 2). The product distribution varies markedly with the triphenylphosphine palladium ratio and the unsaturated alcohol is the main product in the presence of excess palladium over triphenylphosphine and *vice versa*. Thus, the relative extent of these two pathways depends on the triphenylphosphine:palladium ratio.

The reactivity of perfluoroacetone or the α-diketones can simply be explained in terms of their strength of coordination to the catalyst during the initial step of the reaction.† A simple ketone might be weakly bound, thus, acetone or 2-butanone are inert.

* In the palladium catalyzed telomerization reaction of butadiene with nucleophiles such as an alcohol,[10] an amine,[10] a phenol,[16] or active methylene compounds,[17] nucleophiles preferrentially attack the less substituted position of the π-allyl system.

† Palladium complexes containing perfluoroacetone as ligand have been known.[18] This ketone would also be more strongly coordinated to palladium than simple ketones.



EXPERIMENTAL

B.ps and m.ps are uncorrected. NMR spectra were measured on a Varian A 60 or HA 100 spectrometer (CCl_4). Mass spectra were recorded on a Hitachi RMU 6A or RMS 4 (coupled to GLPC) mass spectrometer and figures given in parenthesis refer to the relative intensities of the ions concerned. A Yanagimoto GC 550 research chromatograph was used for GLPC. IR spectra were determined on a Hitachi EPI S2 spectrometer. All aldehydes were freshly distilled prior to use.

Reaction of benzaldehyde with butadiene. To a mixture of benzaldehyde (21·0 g), dichlorobis(triphenylphosphine) palladium (0·50 g), and NaOPh (1·30 g) in an autoclave was introduced butadiene (50 ml) and the suspension shaken at 100° for 6 hr. The mixture was diluted with ether (150 ml), water washed, and freed of solvent. The residue was distilled giving pale yellow oil (28 g), b.p. 110–140°/4 mm, consisting of unsaturated alcohol I and four stereoisomers of pyran II in the molar ratio I/II A/II B/II C = 10:23:41:26 (GLPC).

This mixture was redistilled at reduced pressure through a spinning band column. The first fraction (18 g, b.p. 110–125/3 mm) was a mixture of the four stereoisomeric pyrans (II). Chromatography (silicic acid, $CHCl_3$) of this mixture furnished isomer II B (*ca.* 6 g) from the less polar fraction, and rechromatography (alumina, hexane–ether) of the more polar fraction, gave II A and II C separately. Attempted purification of the final isomer II D, the presence of which was detected by GLPC, was not successful. Stereochemistry of each isomer was assigned by NMR (discussed above).

2-Phenyl-*trans*-3, *cis*-6-divinyltetrahydropyran (II A): IR(liquid film) 1645 (olefin), 1145, 1130, 1090, 1064, 1028 (ether), 990, 915 (olefin); *m/e* 214, 108, 107, 105, 93, 91, 80, 79, 77, 67, 54(100), 41, 39; NMR, (Table IV). (Found: C, 84·20; H, 8·37. Calc. for $C_{15}H_{18}O$: C, 84·07; H, 8·47%.)

2-Phenyl-*cis*-3, *cis*-6-divinyltetrahydropyran (II B): IR(liquid film) 1642 (olefin), 1195, 1180, 1130, 1110, 1095, 1075, 1063, 1030 (ether), 990, 910 (olefin); *m/e* 214, 108, 107, 105, 93, 91, 80, 79, 77, 67, 54(100), 41, 39; NMR, (Table IV). (Found: C, 83·79; H, 8·50. Calc. for $C_{15}H_{18}O$: C, 84·07; H, 8·47%.)

2-Phenyl-*cis*-3, *trans*-6-divinyltetrahydropyran (II C): IR(liquid film) 1645(olefin), 1190, 1125, 1110, 1040, 1030, 1015(ether), 995, 915(olefin); *m/e* 214, 108, 107, 105, 93, 91, 80, 79, 77, 67, 54(100), 41, 39; NMR, (Table IV). (Found: C, 83·88; H, 8·40. Calc. for $C_{15}H_{18}O$: C, 84·07; H, 8·47%.)

Further distillation afforded alcohol I(1·1 g) as colourless viscous oil: b.p. 130–4°/3 mm: IR(liquid film) 3444, 1645, 1190, 1175, 1080, 1057, 1037, 1025, 995, 910; NMR 7·4–8·0 (3), 6·73(1), 5·54(1), 3·3–5·2(8), 2·81(5). (Found: C, 84·01; H, 8·48. Calc. for $C_{15}H_{18}O$: C, 84·07; H, 8·47%.)

Conversion of the pyran II *to* 3-*benzyloctane.* A suspension of pyran II (10 g) and palladium black (0·1 g) in EtOH containing 1% HCl (40 ml) was shaken under H_2 (3 atom) at 50° for 12 hr. After work-up and distillation, 6-benzyl-3-octanol was obtained as a colourless oil (8·1 g): b.p. 115–120/4 mm; *m/e* 220(M^+); NMR 9·12(t, 4), 8·64(m, 9), 2·90(m, 5). (Found: C, 81·46; H, 10·83. Calc. for $C_{15}H_{24}O$: C, 81·76, H, 10·98%.)

6-Benzyl-3-octanone was prepared by Jone's oxidation of the above alcohol as a pale yellow oil (80%): b.p. 110–115/3 mm; *m/e* 218, 146, 127, 117, 92, 91, 85, 72, 57, 65. 2,4-Dinitrophenylhydrazone: m.p. 92° (hexane). (Found: C, 63·39; H, 6·68; N, 14·00. Calc. for $C_{21}H_{26}N_4O_4$: C, 63·39; H, 6·58; N, 14·06%.)

A mixture of the above prepared 6-benzyl-3-octanone(0·90 g), KOH (1·5 g), and hydrazine hydrate (1 ml, 80%) in ethylene glycol(15 ml) was heated at 120° for 6 hr, and 200–220° for 3 hr. The crude isolated product was distilled to furnish 3-benzyloctane as a mobile liquid(0·65 g, 92% purity by GLPC): b.p. 145–8 /30 mm. An analytical sample was obtained by prep GLPC, *m/e* 204, 112, 92, 91, 71, 65, 57, 43, 41, 29. (Found: C, 87·91; H, 11·91. Calc. for $C_{15}H_{24}$: C, 88·16; H, 11·84.) The same compound was prepared by hydrogenation (acidic medium) of alcohol I using palladium black as catalyst in 75% yield, the two products were identical in all respects.

Reaction of furfural with butadiene. Furfural (20 g), dichlorobis (triphenylphosphine)palladium (0·4 g) and NaOPh (0·55 g) were reacted with butadiene (50 ml) as described above at 70° for 44 hr to give a colorless oil (32·6 g) after distillation, b.p. 85–115°/2 mm. Analytical GLPC revealed the presence of three isomeric pyrans of IX and unsaturated alcohol X in the ratios IX A/IX B/IX C/X = 22:29:34:15.

This mixture was redistilled at reduced pressure through a spining band column. The first fraction (22 g, 85–95°/3 mm) was a mixture of the three isomeric pyrans of IX, of which two pyrans, IX A and IX C, were separated by repeated chromatography (silic acid with $CHCl_3$). Stereochemical assignments of each isomer were performed by NMR analysis as described above (Table IV). Although unresolved by chromatography, the third component was the isomeric pyran IX, clearly revealed by the mass assay.

2-Furyl-*cis*-3-*cis*-6-divinyltetrahydropyran(IX A): IR(liquid film) 1640, 990, 910(vinyl), 1110, 1070, 1040(ether): NMR(Table IV): *m/e* 204(1·0), 108(2·6), 97(35), 96(14), 95(13), 80(6·5), 79(13), 67(20), 55(9·9), 54(100), 41(13), 39(19). (Found: C, 76·27; H, 7·95. Calc. for $C_{13}H_{16}O_2$: C, 76·44; H, 7·90%.)

2-Furyl-*trans*-3-*cis*-6-divinyltetrahydropyran (IX C): IR(liquid film) 1644, 990, 910(vinyl), 1060(ether), 730(furan): NMR(Table IV): *m/e* 204(1·0), 108(3·3), 97(40), 96(14), 95(14), 80(7·3), 79(15), 67(20), 66(7·6), 55(11), 54(100), 41(14), 39(21). Found: C, 76·30; H, 7·91. Calc. for $C_{13}H_{16}O_2$: C, 76·44; H, 7·90%).

2-Furyl-3,6-divinyltetrahydropyran(IX B): MS/GLPC *m/e* 204(1·2), 108(4·0), 97(42), 96(14), 80(7·2), 79(15), 67(21), 66(9·1), 55(13), 54(100), 41(12), 39(22).

Further distillation afforded alcohol X(6·1 g), b.p. 98–115°. An analytical sample was obtained by redistillation yielding 1-furyl-2-vinyl-4,6-heptadien-1-ol as a colorless clear oil: IR(liquid film) 3400, 1010–1000, 990, 910: NMR 7·28–8·01(3), 7·04(1), 5·49(1), 3·3–5·2(8), 3·80(2), 2·74(1).

Reaction of acetaldehyde with butadiene. (a) *In the absence of base.* A solution of acetaldehyde (44 g), palladium acetate(0·22 g), and tri-phenylphosphine (1·31 g) in isopropanol (70 ml) was treated with butadiene (160 ml), and the mixture shaken at 60–70° for 17 hr. The resulting oil was distilled to afford a colorless oil (106 g), b.p. 70–100°/40 mm, the GLPC analysis of which revealed the four isomeric pyrans of XI(XI A/XI B/XI C/XI D = 46:32:6:16). None of the corresponding unsaturated alcohol was obtained under these conditions. The mixture was submitted to repeated column chromatography (silicic acid, $CHCl_3$) providing analytical samples of two pyrans, IX C and IX D.

2-Methyl-*trans*-3, *trans*-6-divinltetrahydropyran (IX C): IR(liquid film) 1645, 1130, 1120, 1098, 1050, 1000, 915, 883 cm^{-1}: NMR, (Table IV): *m/e* 152(vw), 108(5·5); 93(8·6), 80(12), 79(21), 67(26), 66(17), 55(14), 54(100), 53(9·4), 43(14), 41(15), 39(19). (Found: C, 78·81; H, 10·52. Calc. for $C_{10}H_{16}O$: C, 78·89; H, 10·59%.)

2-Methyl-*cis*-3, *trans*-6-divinyltetrahydropryan (IX D): IR(liquid film) 1643, 1127, 1083, 1042, 993, 915, 881, 868 cm^{-1}.): NMR, (Table IV): *m/e* 152(vw), 108(4·8), 93(9·6), 80(11), 79(20), 67(27), 66(15), 55(13), 54(100), 53(8·4), 43(11), 41(14), 39(20). Found: C, 78·70; H, 10·72. Calc. for $C_{10}H_{16}O$: C, 78·89; H, 10·59%.)

The mass spectra of the other two pyrans, IX A and IX B, were obtained using MS/GLPC combination: IX A(*m/e* 152(vw), 108(4·9), 93(7·3), 80(10), 79(18), 67(20), 66(14), 55(11), 54(100), 53(7·0), 43(9·4), 41(11), 39(15). IX B(*m/e* 152(vw), 108(4·8), 93(6·8), 80(9·2), 79(17), 67(20), 66(13), 55(10), 54(100), 53(7·5), 43(11), 41(12), 30(16)).

(b) *In the presence of base.* The reaction was carried out as described above using acetaldehyde (11 g), benzene (30 ml), dichlorobis(triphenylphosphine) palladium (0·35 g), NaOPh (1 g), and butadiene (60 g). The crude product obtained on extractive work-up was distilled to provide, after a forerun containing the pyran IX(7·6 g), a clear colorless liquid (14 g), b.p. 80–140°/5 mm, consisting of dioxane XII as major component (*ca.* 40 rel %). An analytical sample was obtained by fractional distillation furnishing 2,4-

dimethyl-6-(2,7-octadienyloxy)-1,3-dioxane(XII) as a clear viscous oil: b.p. 124°/5 mm: IR(liquid film) 1642, 994, 920(mono-substituted olefin); 960(di-substituted olefin), 1155, 1130, 1112, 1040(ether): NMR, 8·85 (3, d, J = 6), 8·77(3, d, J = 5·2), 8·2–8·7(4, m), 7·96(4, m), 6·34(1, m), 6·06(1), 5·76(1), 5·35(1, q, J = 5), 5·42(1, q), 5·09(1), 5·05(1), 4·0–4·64(3): *m/e* 240, 115, 109, 93, 79, 71, 67, 45, 43, 41, 39. (Found: C, 70·01; H, 10·05. Calc. for $C_{14}H_{24}O_3$: C, 69·96; H, 10·07%).

Reaction of n-propionaldehyde with butadiene. 2-Ethyl-3,6-divinyltetrahydropyran (XIII) was prepared as described above (55%). IR(liquid film) 1640, 1110, 1035, 990, 910. The mass spectra of four stereoisomers of XIII were obtained using a MS/GLPC apparatus, and major fragments from each isomer displayed the same pattern: *m/e* (rel intensity for XIII A, XIII B, XIII C, and XIII D, respectively) 166 (vw), 108(13, 14, 11, 12), 93(15, 14, 16, 13), 80(18, 16, 16, 12), 79(28, 30, 28, 25), 67(25, 26, 29, 26), 66(15, 14, 15, 10), 57(15, 16, 17, 12), 55(12, 11, 15, 11), 54(100, 100, 100, 100), 41(14, 13, 15, 15), 39(16, 16, 14, 12).

Reaction of n-butyraldehyde with butadiene. 2-n-Propyl-3,6-divinyltetrahydropyran(XIV) was prepared as described above (b.p. 110–120/40 mm, 62%). IR(liquid film) 1640, 1120, 1100, 1075, 1045, 990, 910. The mass spectra of four stereoisomers of XIV were obtained using MS/GLPC, and major fragments from each isomer displayed the samer pattern: *m/e* (rel intensity for XIV A, XIV B, XIV C, and XIV D, respectively) 180(vw), 108(15, 13, 11, 13), 93(17, 14, 17, 17), 80(20, 16, 18, 24), 79(32, 26, 24, 37), 71(16, 15, 10, 12), 67(26, 22, 27, 32), 66(18, 14, 16, 19), 55(14, 12, 14, 13), 54(100, 100, 100, 100), 41(18, 15, 14, 20), 39(14, 16, 15, 16).

Reaction of isobutyraldehyde with butadiene. (a) *Using palladium catalyst* 2-iso-Propyl-3,6-divinyltetrahydropyran (XV) was obtained by the procedure described above (b.p. 90–110/35 mm, 30%). The three isomeric pyrans XV were separated as above and assignments of each structure were performed by NMR analysis, (Table IV).

2-iso-Propyl-*trans*-3, *cis*-6-divinyltetrahydropyran(XV A): IR(liquid film) 1643, 990, 910(olefin); 1050, 1040(ether): NMR, (Table IV): *m/e* 180(vw), 108(6·9), 93(10), 80(12), 79(24), 71(12), 67(25), 66(15), 55(13), 54(100), 53(7·4), 43(19), 41(17), 39(15). (Found: C, 79·76; H, 11·00. Calc. for $C_{12}H_{20}O$: C, 79·94; H, 11·18%.)

2-Isopropyl-*cis*-3, *cis*-6-divinyltetrahydropyran(XV B): IR(liquid film) 1640, 998, 910(olefin), 1080, 1046, 1032(ether): NMR, (Table IV): *m/e* 180(vw), 108(7·0), 93(12), 80(14), 79(29), 71(14), 67(27), 66(15), 55(15), 54(100), 53(7·9), 43(19), 41(19), 39(15). (Found: C, 79·70; H, 11·02. Calc. for $C_{12}H_{20}O$: C, 79·94; H, 11·18%.)

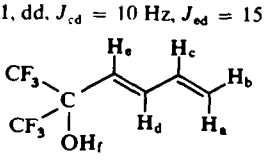
2-Isopropyl-*cis*-3, *trans*-6-divinyltetrahydropyran(XV D): IR(liquid film) 1645, 998, 910(olefin), 1045, 1015(ether): NMR, (Table IV): *m/e* 180(vw), 108(5·0), 93(11), 80(12), 79(27), 81(12), 67(39), 66(14), 55(17), 54(100), 53(7·0), 43(21), 41(24), 39(18). (Found: C, 79·81; H, 11·09. Calc. for $C_{12}H_{20}O$: C, 79·94; H, 11·18%.)

The mass spectrum of isomer XV C was obtained using MS/GLPC and displayed the same fragment pattern as the other isomers: *m/e* 180(vw), 108(6·5), 93(9·0), 80(11), 79(21), 71(11), 67(31), 66(15), 55(15), 54(100), 53(7·3), 43(20), 41(21), 39(16).

(b) *Using platinum catalyst.* A mixture of isobutyraldehyde(14·4 g), dichlorobis(triphenylphosphine)-platinum(0·79 g) of NaOPh(1·16 g), and butadiene(21·6 g) was shaken at 90° for 17 hr. The mixture was distilled to furnish, after a forerun of XV(1·7 g), 2,6-diisopropyl-5,5-dimethyl-1,3-dioxan-4-on(XVI) as a colourless viscous oil(8·4 g, 58%): IR(liquid film) 1740, 1250(lactone): 1170, 1140, 1000(ether): NMR, 9·00(6, d, J = 6), 8·97(6, d, J = 6), 8·97(6, d, J = 6), 8·71(6), 8·08(1), 8·01(1), 5·74(1, d, J = 5·5), 4·92(1, d, J = 4). (Found: C, 67·28; H, 10·28. Calc. for $C_{12}H_{22}O_3$: C, 67·25; H, 10·35%.)

Reaction of perfluoroacetone with butadiene. A mixture of perfluoroacetone(25 ml), t-BuOH(50 ml), benzene(20 ml), palladium acetate (0·49 g), triphenylphosphine(1·57 g), and butadiene(80 g) was shaken at 40° for 20 hr. The crude product obtained on extractive work-up was distilled to afford, after a forerun containing a small amount of 1,3,7-octatriene, the following two fractions. The first (30·5 g), b.p. 50–67°/70 mm, consisted of 1,3,7-octatriene(57 rel %), t-BuOH (31 rel %), the alcohol XX(5 rel %), and 2,2-trifluoromethyl-2,3-dihydropyran(XVIII, 7 rel %, indentical to an authentic sample[11]). Analytical sample of XX was obtained by prep GLPC.

1,1,1-Trifluoro-2-trifluoromethyl-*trans*-3,5-pentadien-2-ol (XX): IR:(liquid film) 3500, 1310, 1290, 1220, 1189, 1160, 1140 cm^{-1}: NMR, 4·62(1, d, J_{ac} = 17 Hz, H_a), 4·71(1, d, J_{bc} = 10 Hz, H_b), 3·65(1, dd, J_{bc} = 10 Hz, J_{cd} = 10 Hz, H_c), 3·26(1, dd, J_{cd} = 10 Hz, J_{ad} = 15 Hz, H_d), 4·30(1, d, J_{cd} = 15 Hz, H_e),



6·30(1, s, H_f): mass *m/e* 220, 151, 103(base peak), 69, 59, 53, 39. (Found: C, 38·36; H, 3·03. Calc. for $C_7H_6F_6O$: C, 38·16; H, 2·73%.) GLPC analysis showed predominantly a single peak (95% *trans*). The second fraction(46·5 g), b.p. 70–100°/70 mm, consisted of the pyran XVII and the Diels–Alder adduct XIX(3:1 by GLPC). Pyran XVII was separated by repeated distillation, (during which XIX decomposed gradually) as a clear colorless liquid: b.p. 101–105°/72 mm; IR(liquid film) 1642, 1290, 1255, 1210, 1130, 1065, 1045, 1010, 995, 925, 870, 725 cm^{-1}: *m/e* 274, 245, 205, 121, 101, 99, 93, 84, 83, 79, 69, 67, 55, 54, 41, 39: NMR 7·8–8·7(4), 6·33(1), 5·86(1), 4·77–5·07(4), 3·95–4·45(2). (Found: C, 48·43; H, 4·77. Calc. for $C_{11}H_{12}F_6O$: C, 48·18; H, 4·38%.)

Reaction of biacetyl with butadiene. A solution of biacetyl (8·6 g), triphenylphosphine(0·92 g) and palladium acetate (0·22 g) in t-BuOH (20 ml) was treated with butadiene (21 g) at 80° for 17 hr. The crude isolated product was distilled to give, after a forerun containing a small amount of 1,3,7-octatriene(*ca.* 3 g), 2-acetyl-2-methyl-3,6-divinyltetrahydropyran(XXII) as a colorless mobil oil(7 g): b.p. 110–120/3 mm; IR(liquid film) 1720, 1642, 1118, 1110, 1060, 1030, 1015, 990, 915 cm^{-1} (similar absorption as those of 2-alkyl-3,6-divinyltetrahydropyran series except at carbonyl region, see above): NMR 8·99, 8·80, 8·75, and 8·66(4s, 3, MeC—O of four stereoisomers), 7·69, 7·80, and 7·35(3s, 3, MeC=O of four stereoisomers). GLPC analysis showed four peaks, and the mass spectra of each peak were obtained using MS/GLPC: *m/e* (rel intensity for XXII A, XXII B, XXII C, and XXII D, respectively) 194(vw), 152(1·7, 1·7, 1·8, 1·6), 151(9·0, 7·7, 6·8, 9·7), 107(6·9, 6·6, 4·5, 6·2), 93(13, 12, 11, 15), 91(4·8, 4·6, 4·0, 3·8), 86(1·7, 1·8, 6·8, 8·3), 81(4·6, 4·5, 4·0, 4·8), 80(1·9, 1·8, 5·2, 8·3), 79(9·8, 8·2, 12, 19), 71(7·7, 7·3, 6·3, 7·0), 67(41, 42, 39, 35), 55(9·2, 9·1, 9·1, 8·6), 54(46, 44, 31, 30), 53(5·6, 5·9, 6·3, 8·1), 43(100, 100, 100, 100), 41(14, 14, 14, 18), 39(11, 9·6, 13, 16). (Found: C, 74·50; H, 9·41. Calc. for $C_{12}H_{18}O_2$: C, 74·23; H, 9·28%.)

Reaction of benzil with butadiene. A mixture of benzil(3·0 g), t-BuOH(50 ml), benzene(30 ml), butadiene (20 ml), palladium acetate(0·22 g), and triphenylphosphine(0·92 g) was shaken at 50° for 72 hr. The mixture, after usual work-up, was distilled to remove butadiene oligomers (trimer: 4·4 g, b.p. 65°/2 mm; tetramer: 2·0 g, b.p. 110–120°/2 mm). The residual oil was chromatographed (aluminium oxide, hexane–ether) to afford 2-phenyl-2-benzoyl-3-6-divinyltetrahydropyran(XXI) as a colorless viscous liquid(6 g), 63% based on benzil): IR(liquid film) 1678, 1056, 1027, 995, 911, 740, 700, 675 cm^{-1} (similar absorptions as those of II except at carbonyl region, see above). (Found: C, 82·81; H, 7·12. Calc. for $C_{22}H_{22}O_2$: C, 83·02; H, 6·92%.)

REFERENCES

1 Part XLVI, S. Hosaka and J. Tsuji, *Tetrahedron* **27**, 3821 (1971)
2 J. Tsuji and K. Ohno, *Synthesis* 157 (1969)
3 J. Tsuji and K. Ohno, *J. Am. Chem. Soc.* **90**, 94 (1968)
4 R. F. Heck, *Acc. Chem. Res.* **2**, 10 (1969)
5 K. Ohno, T. Mitsuyasu and J. Tsuji, *Tetrahedron Letters* 67 (1971)
6 P. Hayns, *Ibid.* 3687 (1970)
7 R. M. Manyik, W. E. Walker, K. E. Atkins and E. S. Hammack, *Ibid.* 3813 (1970)
8 K. Ohno and J. Tsuji, *Chem. Comm.* 247 (1971)
9 P. S. Shantarovich, V. D. Larionova and Yu. V. Kissin., *Zh. Obs. Khim.* **36**(5), 794 (1966)
10 S. Takahashi, T. Shibano and N. Hagihara, *Bull. Chem. Soc. Japan* **41**, 454 (1968)
11 Y. V. Zeifman, N. P. Gambaryan and I. L. Knunyants., *Izv. Akad. Nauk SSSR, Ser. Khim.* 1472 (1965)
12 P. Heimbach, P. W. Jolly and G. Wilke, *Advances in Organometallic Chemistry* vol. 8 p. 39. Academic press
13 J. A. Pople, W. G. Schneider and H. J. Bernstein *High-Resolution Nuclear Magnetic Resonance.* p. 218. McGraw-Hill, New York
14 R. U. Lemieux, R. K. Kulling, H. J. Bernstein and W. G. Schneider, *J. Am. Chem. Soc.* **80**, 6098 (1958)
15 S. Takahashi, H. Yamazaki and N. Hagihara, *Bull. Chem. Soc. Japan* 254 (1968)
16 E. J. Smutny, *J. Am. Chem. Soc.* **89**, 6793 (1967)
17 G. Hata, K. Takahashi and A. Miyake, *Chem. Ind.* 1836 (1969)
18 B. Clark, R. B. L. Osborn, M. Green and F. G. A. Stone, *J. Chem. Soc.* (A) 168 (1968)