Dimerization of Isoprene by Palladium-Diphosphine Complex Catalyst

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Oligomerization of isoprene catalyzed by the $PdBr_2(Ph_2PCH_2CH_2PPh_2)_2$–PhONa catalyst was studied. The catalyst activity was greatly enhanced by the addition of phenol. Five linear dimers were identified. Distribution of the isomeric dimers was remarkably affected by the molar ratio of phenol to isoprene. The reaction in the presence of a small amount of phenol (phenol/isoprene=1/30) gave 2,7-dimethyl-1,*trans*-3,7-octatriene derived from a tail-to-tail dimerization almost selectively, while the addition of a large amount of phenol (phenol/isoprene=1/1.5) afforded head-to-head dimers (2-vinyl-5-methyl-1,6-heptadiene and 3,6-dimethyl-1,*cis*-3,7-octatriene) as main dimers (more than 40% of all the dimers). In a 1 : 3 ratio of phenol to isoprene the dimers consisted of mainly 2,6-dimethyl-1,*trans*-3,7-octatriene derived from a head-to-tail dimerization.

It is well-known that oligomerization of 1,3-butadiene to cyclic or linear products is catalyzed by some transition metal complexes. A new type of linear dimerization of 1,3-butadiene catalyzed by transition metal compounds of group VIII of the periodic table, completed by addition of a compound having at least one active hydrogen atom to give 2,7-octadienyl derivatives as main products, has recently been found.[1–6] In this reaction palladium complexes, especially palladium-triphenylphosphine complexes, are the most effective.

In connection with the above reaction, we have found[7] that the reaction of 1,3-butadiene with active methylene compounds or amines catalyzed by palladium-diphosphine complexes gives 1 : 1 adducts of 1,3-butadiene to the active methylene compounds or the amines. This type of reaction was not applicable to other active hydrogen compounds such as phenol, alcohols and carboxylic acids, but the reaction in phenol was found to give a linear dimer 1,3,7-octatriene in a good yield. Further research has led us to find that a palladium-diphosphine complex catalyst shows a high catalytic activity in the linear dimerization of 1,3-butadiene and isoprene by addition of a catalytic amount of phenol.

The present paper deals with the dimerization of isoprene in the presence of $PdBr_2$ $(Ph_2PCH_2CH_2PPh_2)_2$, PhONa and PhOH as a catalyst system. Some catalysts containing chromium,[8] titanium,[9] hafnium,[10] and zirconium[11] have been reported to give linear dimers along with other oligomers. Zerovalent palladium-triphenylphosphine complexes have been also reported[12] to catalyze the reaction in 2-propanol to afford 2,7-dimethyl-1,3,7-octatriene almost selectively.

The reaction of isoprene catalyzed by a combination of $PdBr_2(Ph_2PCH_2CH_2PPh_2)_2$, PhONa and a small amount of phenol also gave 2,7-dimethyl-1,3,7-octatriene almost selectively, but it was found that by adding a large amount of phenol the reaction afforded 2,6-dimethyl-1,3,7-octatriene as the main product and other linear isomers as minor products.

The results given below deal with our work to determine the structure of the isomeric dimers of isoprene and to investigate the effect of phenol on the distribution of the isomers.

Experimental

Reagent. Isoprene was dried on calcium chloride and distilled under an argon atmosphere. Phenols were purified by distillation. Dibromobis(ethylenebisdiphenylphosphine) palladium (II) was prepared according to the procedure given by Chatt *et al.*[13]

Analysis. Gas-chromatography was used for identification and quantitative analysis. A squalane-on-Celite column and a Silicone DC 550 capillary column (a length: 90 feet, a diameter: 0.02 inch) were used. 4-Vinyl-cyclohexene was used as an internal standard. A preparative gas-chromatography apparatus equipped with a squalane-on-Celite column was used to isolate the products. IR, NMR, UV and mass spectra were also used to identify the products. Samples for the measurement of mass spectra were introduced directly to the mass spectrophotometer from gas-chromatography apparatus equipped with a capirally column.

General Procedure for the Dimerization of Isoprene. To a 100 ml stainless steel autoclave, $PdBr_2(Ph_2PCH_2CH_2PPh_2)_2$, PhONa, PhOH, isoprene and benzene were charged under an argon atmosphere. The autoclave was heated at 150°C with stirring.

Results and Discussion

The dimerization of isoprene catalyzed by a combination of $PdBr_2(Ph_2PCH_2CH_2PPh_2)_2$, PhONa and a small amount of PhOH gave a linear dimer almost

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[1] S. Takahashi, T. Shibano, and N. Hagihara, *Tetrahedron Lett.*, **1967**, 2451.

[2] S. Takahashi, T. Shibano, and N. Hagihara, This Bulletin, **41**, 454 (1968).

[3] E. J. Smutny, *J. Amer. Chem. Soc.*, **89**, 6793 (1968).

[4] E. J. Smutny, H. Chung, K. C. Dewhirst, W. Keim, T. M. Shryne ,and H. E. Thyret, Preprints of Symposium on Homogeneous Catalytic Reactions Involving Palladium, B100 (1969).

[5] G. Hata, K. Takahashi, and A. Miyake, *Chem. Ind.* (London), **1969**, 1836.

[6] G. Hata, K. Takahashi, and A. Miyake, *J. Org. Chem.*, **36**, 2116 (1971).

[7] K. Takahashi, A. Miyake, and G. Hata, This Bulletin, **45**, 1183 (1972).

[8] G. Wilke, *J. Polym. Sci.*, **38**, 45 (1959).

[9] J. Itakura and H. Tanaka, *Makromol. Chem.*, **123**, 274 (1969).

[10] A. Misono, Y. Uchida, K. Furuhata, and S. Yoshida, This Bulletin, **42**, 1383 (1969).

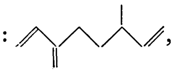
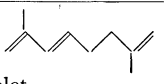
[11] A. Misono, Y. Uchida, K. Furuhata, and S. Yoshida, *ibid.*, **42**, 2303 (1969).

[12] S. Takahashi, T. Shibano, and N. Hagihara, Preprints of 24th Symposium on Catalysts, p. 4 (1969).

[13] J. Chatt, F. A. Hart, and H. R. Watson, *J. Chem. Soc.*, **1962** 2537.

Table 1. Spectral and physical properties of the products

Product[a)]	NMR[b)] (τ)	IR (cm^{-1})	UV[c)] (mμ)	bp (°C)	n_D^{25}
A	9.03(3H, d, J=6.0 Hz), 8.58(2H, m), 8.2—7.7(3H, m), 5.20(2H, m), 5.12(2H, s), 5.03(1H, m), 4.78(1H, m), 4.40(1H, m), 3.72(1H,q, J=18.5 Hz, 11.0 Hz).	1644, 1612, 992, 908, 891	225(ε 18000)	161	1.4570
B	9.06(3H, d, J=6.0 Hz), 8.28(3H, s), 7.9(3H, m), 4.1—5.3(6H, m), 3.96(1H,d, J=16.0 Hz)	1644, 1612, 991, 962, 910, 881	230(ε 24000)	167	1.4704
E	8.30(3H, s), 8.22(3H, s), 7.9(4H, m), 5.36(2H, s), 5.22(2H, s), 4.5(1H, m), 3.94(1H, d, J=17.0 Hz)	1650, 1613, 963, 883	230(ε 25000)	176	1.4721

a) A: , B: , E: 

b) s: singlet, d: doublet, q: quartet, m: multiplet.

c) Measured in ethanol.

selectively. On the other hand, the reaction in the presence of a large amount of PhOH afforded various linear dimers. It was also found that the distribution of linear dimers was remarkably affected by the amount of phenol added. The gas chromatography of the dimers carried out with a 90 feet Silicone DC 550 capirally column is shown in Fig. 1.

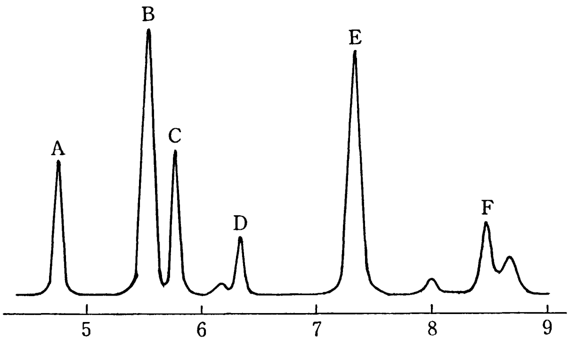
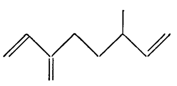
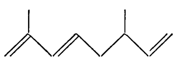


Fig. 1. Gas-chromatograph of isoprene dimers column: Silicone DC 550 (90 ft, 0.02 in) temperature: 110°C

Products A, B, and E (Fig. 1) were isolated purely and identified by spectroscopic methods. The spectroscopic data are shown in Tables 1 and 2. Products A, B, and E were apparently derived from head-to-head, head-to-tail, and tail-to-tail dimerization of isoprene, respectively.


A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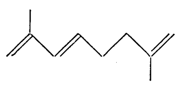
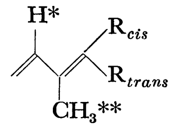
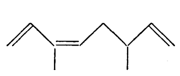

E

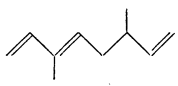
Table 2. Mass spectral data (relative intensities)

m/e	% of base peak				
	A	B	C	D	E
41	78	21	27	25	39
53	36	23	27	24	36
55	31	30	20	17	14
67	46	6	4	5	7
68	100	4	3	3	6
79	10	21	25	23	36
81	15	100	100	100	100
93	26	6	4	4	11
107	22	8	5	4	11
121	10	9	5	4	17
136	2	3	3	4	3

Product C was separated as a mixture with product D. Hydrogenation of the mixture gave only one product, 3,6-dimethyloctane, which was confirmed by the vpc equipped with a capillary column. The NMR spectrum of the mixture showed characteristic signals at τ 3.30 and 3.70 (two quartets, 1H), and τ 8.19 and 8.30 (two singlets, 3H). The intensity ratio of the lower chemical shift to the higher in each pair coincided with the weight ratio of C to D involved in the sample for the measurement of the NMR spectrum. This indicates that the signals at τ 3.30 and 8.19 are due to C and other signals to D. The chemical shifts due to H* and H** of *cis* form in the following general fomula are lower (H*: 20—40 Hz,[14)] H**: 0.07 Hz[15)]) than those of the *trans* form. On the other hand, the mass spectra of C and D were equal (Table 2). Thus, the structures of C and D were presumed as 3,6-dimethyl-1, *cis*-3,7-octatriene and 3,6-dimethyl-1, *trans*-3,6-octratriene, respectively.




C


D

Product F was identified as a mixture of 1-methyl-4-(2-propenyl)cyclohexene and 1-methyl-3-(2-propenyl)-cyclohexene, which were derived from the Diels-Alder reaction of isoprene by spectroscopic measurements. Other products were not identified.

The effect of phenol on the distribution of the isomeric dimers was investigated and the results are summarized in Table 3. The reaction in the absence

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[14)] C. G. Cardenas, *Tetrahedron Lett.*, **1969**, 4013.

[15)] R. B. Bates and D. M. Gales, *J. Amer. Chem. Soc.*, **82**, 5749 (1960).

TABLE 3. REACTIONS IN PHENOL[a)]

Phenol mol	Isoprene mol	Conv.[b)] %	Dimers[c)] %	Distribution of isomeric dimers[d)] A	B	C	D	E	F	Others	Trimers[e)] %
0.0	0.3	19	43	—	—	17	trace	26	57	trace	20
0.01	0.3	90	86	—	6	—	—	89	1	1	12
0.05	0.3	96	72	trace	37	1	trace	55	1	6	22
0.1	0.3	95	57	1	60	8	2	28	—	1	24
0.1	0.2	94	58	2	57	15	3	21	trace	2	28
0.2	0.3	75	32	19	34	22	1	9	11	4	34

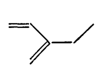
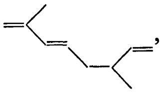
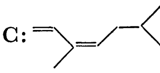
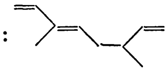
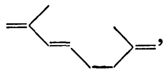
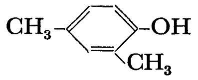
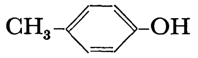
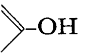
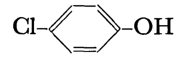
a) Reaction conditions: $PdBr_2(Ph_2PCH_2CH_2PPh_2)_2$ 0.25 mmol, PhONa 2.5 mmol, benzene 15 ml, 150°C, 1 hr.
b) Conversion of isoprene.
c) Based on the conversion of isoprene.
d) A: , B: , C: , D: , E: ,
F: Methylpropenylcyclohexens.
e) Based on the conversion of isoprene.

TABLE 4. EFFECT OF SUBSTITUTED PHENOL ON THE DISTRIBUTION OF DIMERS[a)]

Substituted phenol	Conv.[b)] %	Dimers[c)] %	Distribution of isomeric dimers[d)] A	B	C	D	E	F	Others	Trimers[e)] %
	94	82	trace	26	trace	trace	64	trace	10	12
	93	74	1	46	3	2	38	2	8	24
	95	57	1	60	8	2	27	—	2	24
	13	46	2	1	22	trace	1	71	3	trace

a) Reaction conditions: $PdBr_2(Ph_2PCH_2CH_2PPh_2)_2$ 0.25 mmol, PhONa 2.5 mmol, benzene 15 ml, isoprene 0.3 mol, substituted phenol 0.1 mol, 150°C, 1 hr.
For b), c), d), and e), refer to Table 3

of phenol gave only a small amount of dimers.[16)] However, by adding phenol the catalytic activity was greatly enhanced and linear dimers were afforded in a fairly good yield. With the increase of the amount of phenol, the yield of the dimers decreased while that of the trimers, whose structure was not investigated, increased. It is interesting that the distribution of 2,6-dimethyl-1, *trans*-3,7-octatriene (B), which was derived from the head-to-tail dimerization of isoprene, went up to 60% when 0.1 mol of phenol (to 0.3 mol of isoprene) was added. Further increase of the amount of phenol yielded a considerable amount of the head-to-head dimers (A) and (C) as main products (about 40% in dimers) although the head-to-head addition seems difficult to occur because of repulsion between methyl groups or for some such steric reason. The tail-to-tail isomer 2,7-dimethyl-1, *trans*-3,7-octatriene (E) was given almost selectively in the presence of only a small amount of phenol, but the yield decreased considerably with the increase of phenol. It was confirmed that the variation of the distribution of the isomeric dimers was influenced mostly by the molar ratio of phenol to isoprene.

The results of the investigation on the effect of substituted phenol are shown in Table 4. It is obvious that the effect of substituted groups on the distribution of isomeric dimers and the yield of the dimers is very large. The reaction in the presence of 2,4-xylenol gave linear dimers, mainly 2,7-dimethyl-1, *trans*-3,7-octatriene in a 82% yield. On the other hand, the reaction in *p*-chlorophenol yielded only a small amount of linear dimers, mainly 3,6-dimethyl-1, *cis*-3,7-octatriene, in a 14% yield, the reactivity being much smaller than that in 2,4-xylenol.

[16)] The diphosphine complex $PdBr_2(Ph_2CH_2CH_2PPh_2)_2$ had no catalytic activity. A zero-valent complex $Pd(Ph_2CH_2CH_2PPh_2)_2$ showed low catalytic activity. The catalytic activity of Pd(0) complexes, which is presumed to be similar to that of Pd(II) complexes,[7)] was not studied in detail.