The n.m.r. spectrum had a signal centered at τ 7.51 (assigned to bridge hydrogens in bicyclo[3.3.0]octane,[10] relative area 2), a complex absorption at τ 8.14–8.83 (methylene absorption resembling that in bicyclo[3.3.0]octane,[10] relative area 13), and a well-defined triplet centered at τ 9.03 (methyl H, relative area 3).

Anal. Calcd. for $C_{10}H_{18}$: C, 86.98; H, 13.04. Found: C, 86.90; H, 13.10.

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(10) W. B. Moniz, Ph.D. Thesis, Pennsylvania State University, 1960.

Linear Dimerization of Butadiene with Ferric Chloride–Triphenylphosphine–Triethylaluminum Catalysts

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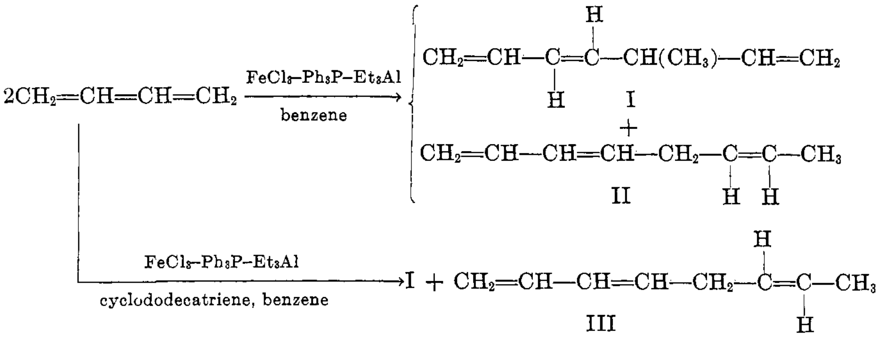
In the previous paper,[1] it has been reported that butadiene has been cyclotrimerized with a novel catalyst system of alkylaluminum halide–titanium tetraalkoxide. Recently, linear dimers of butadiene, 3-methyl-1,4,6-heptatriene and 1,3,6-octatriene, have been produced upon treatment of butadiene with catalyst systems which consisted of combinations of cobalt compounds and trialkylaluminum.[2] We have now found that novel catalyst systems consisting of combinations of ferric chloride, triphenylphosphine, and alkylaluminum compounds are active for linear dimerization of butadiene.

A catalyst was prepared with 1 mole of anhydrous ferric chloride, 1 mole of triphenylphosphine, and 4 moles of triethylaluminum under a nitrogen atmosphere and shaken with butadiene in an autoclave at room temperature overnight. Distillation of the reaction products gave a dimer fraction in 85% yield based on the fixed butadiene, a trimer fraction in about 5% yield, and high boiling oligomers. The dimer fraction consisted of 3-methyl-1,4,6-heptatriene (about 30%) boiling at 115° and 1,3-*cis*-6-octatriene (about 70%) boiling at 129°. Infrared, ultraviolet, and n.m.r. spectra of the methylheptatriene were identical with spectra reported by Otsuka[2a] and Misono.[2b] 1,3-*cis*-6-Octatriene absorbed 3 moles of hydrogen upon catalytic hydrogenation over palladium on charcoal. Its infrared and ultraviolet spectra were identical with those reported by Misono.[2b] The n.m.r. spectrum gave a doublet absorption of the methyl group $(=CH-CH_3)$ and a triplet absorption of the methylene group. The octatriene gave an adduct of maleic anhydride in quantitative yield.



A catalyst which consisted of a combination of *cis,trans,trans*-1,5,9-cyclododecatriene, anhydrous ferric chloride, triphenylphosphine, and triethylaluminum also dimerized butadiene, giving a mixture of 3-methyl-1,4,6-heptatriene and 1,3,6-octatriene fractions. The octatriene fraction boiling at 129° showed infrared absorptions of vinyl and *trans* double bonds and a trace of a *cis* double bond. The ultraviolet spectrum showed that it had two conjugated double bonds. Its n.m.r. spectrum showed absorptions of the methyl group $(=CH-CH_3)$, methylene group, and olefinic protons. The fraction was analyzed by gas chromatography using a tricresyl phosphate column, giving a single peak identical with that of 1,3-*cis*-6-octatriene (II). From these facts, the 1,3,6-octatriene fraction seems to consist of mainly 1,3-*trans*-6-octatriene (III).

The trimer fraction boiling at 140° (15 mm.) absorbed 4 moles of hydrogen upon catalytic hydrogenation over palladium on charcoal and showed infrared absorptions of vinyl, *trans*, and *cis* double bonds. Accordingly, the trimer seems to be linear.

The effects of reaction variables on yields of the dimers have been examined. As summarized in Table I, triethylaluminum and diethylaluminum chloride were equally active. The mole ratio of alkylaluminum compounds to iron compounds must be greater than 3. When the mole ratio was less than 3, little butadiene dimerized and, at a mole ratio of 4 or higher, the reaction rate of butadiene was increased appreciably and the yields of the dimers were greatly improved. The yields remained approximately constant at higher mole ratios. Instead of anhydrous ferric chloride, iron trisacetylacetonate and iron pentacarbonyl were used successfully. By examination of many electron-donor compounds such as ethers, amines, phosphites, and phosphines, it was found that triphenylphosphine gave the most active catalyst and the mole ratio of triphenylphosphine to iron compounds must be 1 or higher. When no electron-donor compound was used, small amounts of polymer were produced instead of the dimers.

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(1) H. Takahasi and M. Yamaguchi, *J. Org. Chem.*, **28**, 1409 (1963).

(2) (a) S. Otsuka, T. Taketomi, and T. Kikuchi, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **66**, 1094 (1963); (b) T. Saito, T. Ono, T. Uchida, and A. Misono, *ibid.*, **66**, 1099 (1963); (c) D. W. Wittenberg, *Angew. Chem.*, **75**, 1124 (1963); (d) S. Tanaka, K. Mabuchi, and N. Simazaki, the 12th Annual Meeting of Polymer Society of Japan, 1963; (e) Studiengesellschaft Kohle m.b.H., Austrian Patent 219,580 (1962). This catalyst consists of a combination of iron trisacetylacetonate, triphenylphosphine, and diethylaluminum ethoxide gave the methylheptatriene, 4-vinylcyclohexene, and small amounts of cyclooctadiene.

TABLE I

LINEAR DIMERIZATION OF BUTADIENE

FeCl$_3$,[a] g.	P:Fe. mole ratio	Al compd.	Al:Fe,[c] mole ratio	Solvent	Temp., °C.	Time, hr.	C$_4$H$_6$, g.	—Dimer fractions[d]—		OT:MHT[e]
								g.	%	
1.0	2	Et$_3$Al	9	Benzene	30	66	146	64	59	...
2.0	1	Et$_3$Al	4	Benzene	32	54	130	76	67	1.6
2.0	1	Et$_3$Al	4	Benzene	30	20	130	62	54	1.8
2.0	1	Et$_3$Al	4	Benzene	17	17	130	78	71	0.5
1.0	1	Et$_3$Al	4	Benzene	17	17	130	83	87	2.0
2.0	1	Et$_3$Al	4	Hexane	13	20	195	111	66	2.3
2.0	1	Et$_2$AlCl	5	Benzene	17	41	163	115	75	1.0
1.5	1	Et$_2$AlCl	6	Benzene	30	43	143	25	71	1.2
1.0	1	Et$_2$AlCl	5	Hexane	13	21	143	86	76	2.3
0.9	0.9[f]	Et$_3$Al	5	Benzene	30	20	130	82	79	1.4

[a] Commercial anhydrous ferric chloride. [b] Mole ratios of triphenylphosphine to ferric chloride. [c] Mole ratios of aluminum compounds to ferric chloride. [d] Yields based on the fixed butadiene. [e] Ratios of 1,3,6-octatriene to 3-methyl-1,4,6-heptatriene in the dimer fractions (analyzed by gas chromatography). [f] Instead of triphenylphosphine, iron pentacarbonyl, Fe(CO)$_5$, was used.

Instead of electron-donor compounds such as triphenylphosphine, metal carbonyl compounds were also used. To a mixture of metal carbonyl compounds and anhydrous ferric chloride, triethylaluminum was added and treated with butadiene, giving a dimer fraction consisting of a mixture of 1,3,6-octatriene and 3-methyl-1,4,6-heptatriene in good yields. The mole ratio of carbonyl group to iron must be 0.5 or higher.

Procedures in which each catalyst component was mixed with each other and butadiene had only minor effects on the yields of the dimers but gave some change in the composition of the dimer fractions. In a case where butadiene was added to a mixture of triethylaluminum, anhydrous ferric chloride, and triphenylphosphine, the 1,3,6-octatriene fraction consisted of 1,3-*cis*-6-octatriene (II) only, but when triethylaluminum was added to a mixture of butadiene, ferric chloride, and triphenylphosphine, the octatriene fraction consisted of a mixture of 1,3-*cis*-6- (II) and 1,3-*trans*-6-octatriene (III).

A characteristic of these catalyst systems is that they give octatriene in better yield than the catalysts containing cobalt compounds. However, the purity of anhydrous ferric chloride has a great effect on the ratio of 1,3,6-octatriene to 3-methyl-1,4,6-heptatriene and the yield of the dimers. When commercial anhydrous ferric chloride was used, the ratio was 0.5–2 and, when anhydrous ferric chloride purified by sublimation was used, the ratio was less than 0.1. Water content of the catalyst systems seems to have a great effect on the ratio and the yield and it is now under investigation. Solvents had some effect on the ratio as follows: the ratio was 2 in cases of benzene and xylene and 3 in cases of cyclohexane and *n*-hexane. Yields of the dimers were better in aromatic than in aliphatic solvents.

Experimental

Linear Dimerization of Butadiene with a Catalyst of FeCl$_3$–Ph$_3$P–Et$_3$Al.—To a mixture of 2 g. of commercial anhydrous ferric chloride, 3 g. of triphenylphosphine, and 50 ml. of benzene, a solution of 6 g. of triethylaluminum in 20 ml. of benzene was added and the whole was treated with 200 ml. (130 g.) of butadiene in an autoclave at room temperature (17°). After 17 hr., the reaction mixture was decomposed with methanol and the inorganic compounds were dissolved with dilute hydrochloric acid. The organic layer was isolated, dried over sodium sulfate, and distilled, giving 86 g. (82% based on the fixed butadiene) of a dimer fraction boiling at 110–130°, 4 g. of a trimer fraction boiling at 135–145° (15 mm.), and 15 g. of residue.

By gas chromatographic analysis it was determined that the dimer fraction consisted of a mixture of 1,3,6-octatriene (66%) and 3-methyl-1,4,6-heptatriene (33%). Redistillation of the fraction gave 3-methyl-1,4,6-heptatriene boiling at 115° and 1,3,6-octatriene boiling at 129°.

3-Methyl-1,4,6-heptatriene [$n^{20}\text{D}$ 1.4656, lit.[2a,b] $n^{20}\text{D}$ 1.4656–1.4657; $\lambda_{\max}^{\text{cyclohexane}}$ 228 mμ (ϵ 2.6 $\times$ 10^4), lit. $\lambda_{\max}$ 228 mμ (ϵ 2.5–2.6 $\times$ 10^4); τ 8.4 (doublet, CH$_3$)] absorbed 3 moles of hydrogen upon catalytic hydrogenation over palladium on charcoal. The infrared, ultraviolet, and n.m.r. spectra of this dimer were identical with those reported by Otsuka, *et al.*,[2a] and Misono, *et al.*[2b]

1,3,6-Octatriene [b.p. 129°; $n^{20}\text{D}$ 1.4743, lit.[2b] $n^{20}\text{D}$ 1.4758; $d^{20}{}_4$ 0.7745; $\lambda_{\max}^{\text{cyclohexane}}$ 228 mμ (ϵ 3.2 $\times$ 10^4), lit.[2b] $\lambda_{\max}$ 228 mμ (ϵ 3.7 $\times$ 10^4); τ 8.4 (doublet, 3H, J = 5.4 c.p.s., CH_3CH=), 7.2 (triplet, 2H, J = 5.5 c.p.s., –CH_2–), and 3.5–5.3 (7H, olefinic protons)] absorbed 3 moles of hydrogen upon catalytic hydrogenation. The infrared spectrum showed absorptions of 1,3-*cis*-6-octatriene at 1640, 1605, 1000, 895, and 705 cm.$^{-1}$.

With FeCl$_3$–Fe(CO)$_5$–Et$_3$Al Catalyst.—To a mixture of 1.0 g. of commercial anhydrous ferric chloride, 1.2 g. of iron pentacarbonyl, and 50 ml. of benzene, 170 g. of butadiene was added and the whole was treated with a solution of 5.5 g. of triethylaluminum in 30 ml. of benzene in an autoclave for 40 hr. The reaction mixture was treated as mentioned above, giving 96 g. (80% yield) of a dimer fraction. The fraction consisted of a mixture of 3-methyl-1,4,6-heptatriene (71%) and 1,3,6-octatriene (28%).

With FeCl$_3$–Ph$_3$P–Cyclododecatriene–Et$_3$Al Catalyst.—A mixture of 2 g. of anhydrous ferric chloride and 3 g. of triphenylphosphine was heated with 10 ml. of *cis, trans, trans*-1,5,9-cyclododecatriene at 120° for 30 min. After cooling, a solution of 7 g. of triethylaluminum in 50 ml. of benzene was added to the mixture and the product was treated with 120 g. of butadiene for 18 hr. Distillation of the product gave 74 g. of a dimer fraction in a 67% yield. Redistillation of the dimer fraction gave 34 g. of 3-methyl-1,4,6-heptatriene boiling at 115° and 31 g. of 1,3,6-octatriene boiling at 129°. The 1,3,6-octatriene fraction [$n^{20}\text{D}$ 1.4719, $d^{20}{}_4$ 0.7762, $\lambda_{\max}^{\text{cyclohexane}}$ 228 mμ (ϵ 3.7 $\times$ 10^4), τ 8.4 (3H, CH_3CH=) and 7.2 (2H, –CH_2–)] showed infrared absorptions of a *trans* double bond (965 cm.$^{-1}$) and a trace of a *cis* double bond (705 cm.$^{-1}$).

Anal. Calcd. for C$_8$H$_{12}$: C, 88.82; H, 11.18. Found: C, 89.10; H, 11.14.

Tetracyclohexylmethane

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Tetracyclohexylmethane has not heretofore been obtained. No synthesis by condensation reactions has