

TABLE I  
 LINEAR DIMERIZATION OF BUTADIENE

FeCl <sub>3</sub> , <sup>a</sup> g.	P: Fe. mole ratio	Al compd.	Al: Fe, <sup>c</sup> mole ratio	Solvent	Temp., °C.	Time, hr.	C <sub>4</sub> H <sub>6</sub> , g.	Dimer fractions <sup>d</sup>		OT:MHT <sup>e</sup>
								g.	%	
1.0	2	Et <sub>3</sub> Al	9	Benzene	30	66	146	64	59	...
2.0	1	Et <sub>3</sub> Al	4	Benzene	32	54	130	76	67	1.6
2.0	1	Et <sub>3</sub> Al	4	Benzene	30	20	130	62	54	1.8
2.0	1	Et <sub>3</sub> Al	4	Benzene	17	17	130	78	71	0.5
1.0	1	Et <sub>3</sub> Al	4	Benzene	17	17	130	83	87	2.0
2.0	1	Et <sub>3</sub> Al	4	Hexane	13	20	195	111	66	2.3
2.0	1	Et <sub>2</sub> AlCl	5	Benzene	17	41	163	115	75	1.0
1.5	1	Et <sub>2</sub> AlCl	6	Benzene	30	43	143	25	71	1.2
1.0	1	Et <sub>2</sub> AlCl	5	Hexane	13	21	143	86	76	2.3
0.9	0.9 <sup>f</sup>	Et <sub>3</sub> Al	5	Benzene	30	20	130	82	79	1.4

<sup>a</sup> Commercial anhydrous ferric chloride. <sup>b</sup> Mole ratios of triphenylphosphine to ferric chloride. <sup>c</sup> Mole ratios of aluminum compounds to ferric chloride. <sup>d</sup> Yields based on the fixed butadiene. <sup>e</sup> Ratios of 1,3,6-octatriene to 3-methyl-1,4,6-heptatriene in the dimer fractions (analyzed by gas chromatography). <sup>f</sup> Instead of triphenylphosphine, iron pentacarbonyl, Fe(CO)<sub>5</sub>, 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<sub>3</sub>-Ph<sub>3</sub>P-Et<sub>3</sub>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*<sub>D</sub><sup>20</sup> 1.4656, lit.<sup>2a,b</sup> *n*<sub>D</sub><sup>20</sup> 1.4656–1.4657; λ<sub>max</sub><sup>cyclohexane</sup> 228 mμ (ε 2.6 × 10<sup>4</sup>), lit. λ<sub>max</sub> 228 mμ (ε 2.5–2.6 × 10<sup>4</sup>); τ 8.4 (doublet, CH<sub>3</sub>) 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.*,<sup>2a</sup> and Misono, *et al.*<sup>2b</sup>

1,3,6-Octatriene [b.p. 129°; *n*<sub>D</sub><sup>20</sup> 1.4743, lit.<sup>2b</sup> *n*<sub>D</sub><sup>20</sup> 1.4758; *d*<sub>4</sub><sup>20</sup> 0.7745; λ<sub>max</sub><sup>cyclohexane</sup> 228 mμ (ε 3.2 × 10<sup>4</sup>), lit.<sup>2b</sup> λ<sub>max</sub> 228 mμ (ε 3.7 × 10<sup>4</sup>); τ 8.4 (doublet, 3H, *J* = 5.4 c.p.s., CH<sub>3</sub>CH=), 7.2 (triplet, 2H, *J* = 5.5 c.p.s., -CH<sub>2</sub>-), 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.<sup>-1</sup>.

**With FeCl<sub>3</sub>-Fe(CO)<sub>5</sub>-Et<sub>3</sub>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<sub>3</sub>-Ph<sub>3</sub>P-Cyclododecatriene-Et<sub>3</sub>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*<sub>D</sub><sup>20</sup> 1.4719, *d*<sub>4</sub><sup>20</sup> 0.7762, λ<sub>max</sub><sup>cyclohexane</sup> 228 mμ (ε 3.7 × 10<sup>4</sup>), τ 8.4 (3H, CH<sub>3</sub>CH=) and 7.2 (2H, -CH<sub>2</sub>-)] showed infrared absorptions of a *trans* double bond (965 cm.<sup>-1</sup>) and a trace of a *cis* double bond (705 cm.<sup>-1</sup>).

*Anal.* Calcd. for C<sub>8</sub>H<sub>12</sub>: 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

been reported and previous attempts to hydrogenate tetraphenylmethane catalytically have resulted in the formation of tricyclohexylmethane and dicyclohexylmethane as major products. No tetracyclohexylmethane was isolated.<sup>1</sup> It has been suggested that the steric requirements of the cyclohexyl group prevent the bonding of four such bulky groups to a single carbon atom.<sup>2</sup>

This laboratory has demonstrated that tetraphenylmethane in the presence of 5% rhodium on charcoal may be catalytically hydrogenated, with surprising ease considering the expected steric situation, at a relatively mild temperature of 100° to give 80% of the theoretical yield of tetracyclohexylmethane, m.p. 282°.

Microanalytical data for carbon and hydrogen are accurate enough to rule out the possibility of residual double bond unsaturation but spectral confirmation seemed desirable in view of slightly low molecular weight values by vapor osmometry (339 and 332, compared to the theoretical 344.6). The ultraviolet absorption spectrum in cyclohexane solution from the visible down to 205 m $\mu$  showed no bond with an absorptivity (molar extinction coefficient) even as great as 2.3 l. mole-cm.<sup>-1</sup>. This very high transparency in this region rules out any possibility of existence of phenyl or conjugated olefinic unsaturation. In addition, the exceedingly simple absorption spectrum taken in carbon tetrachloride solution over the infrared region from 2 to 13  $\mu$  shows no absorption from 4000 to 3000, 2500 to 2000, or 2000 to 1500 cm.<sup>-1</sup>, thus, respectively, ruling out any hydrogen on unsaturated carbon, hydrogen on silicon, and/or any unsaturated bonds to carbon.

Dehydrogenation of tetracyclohexylmethane to tetraphenylmethane can be effected in the presence of 10% palladium on charcoal at temperatures above 259°. However, extensive fragmentation occurs at these conditions. Although the presence of tetraphenylmethane in small amounts in such dehydrogenation reaction mixtures was demonstrated by comparison with an authentic sample through a capillary column gas chromatograph, it was not possible to isolate a useful quantity of the pure compound.

In view of the steric strain involved, tetracyclohexylmethane has demonstrated remarkable thermal stability. Melting occurs at 282° without decomposition. However, the stability in the presence of catalyst is reduced, thereby necessitating relatively mild conditions for hydrogenation. Previous workers<sup>1</sup> appear to have used overly harsh conditions which led to cleavage. These factors probably account for past erroneous conclusions interpreting the steric requirements to be unfavorable to the formation and stability of tetracyclohexylmethane.

Atomic models, Stuart-Briegleb and Fisher-Hirschfelder-Taylor, allow construction of the molecule with difficulty and suggest that the conformations of the cyclohexyl groups may be partially frozen. Stereochemical and X-ray crystal studies to clarify this point are now in progress.

#### Experimental

**Hydrogenation of Tetraphenylmethane.**—Into a 1-l. stainless steel liner were placed 3.2 g. (0.01 mole) of tetraphenylmethane

(K & K Laboratories), 1 g. of 5% rhodium-on-charcoal catalyst, and 150 ml. of methylcyclohexane. The liner was placed inside an American Instrument Co. superpressure rocking reactor and the assembly was flushed three times with hydrogen by pressurization to 1200 p.s.i. and subsequent venting to atmospheric pressure. The assembly was heated to 100° and pressurized to 1250 p.s.i. with hydrogen, and rocking of the assembly was started. After 16 hr., the heat and rocking mechanism were turned off and the assembly was allowed to cool to room temperature. The reaction mixture was filtered through an extraction thimble and the residue was extracted with methylcyclohexane for 8 hr. in a Soxhlet apparatus. The solvent was removed under vacuum and the residue was recrystallized twice from cyclohexane. After overnight drying at 100° in a vacuum oven there was obtained 2.75 g. (80% of theory) of tetracyclohexylmethane, m.p. 282°.

*Anal.* Calcd. for C<sub>25</sub>H<sub>44</sub>: C, 87.13; H, 12.87; mol. wt., 344.6. Found: C, 87.35; H, 12.87; mol. wt. (Mechrolab osmometer), 339, 332.

Moderate-to-strong infrared absorption peaks in the 2–13- $\mu$  region for solutions in carbon tetrachloride were observed in a Perkin-Elmer Model 521 spectrophotometer at (in cm.<sup>-1</sup>) 2920 (3.42  $\mu$ ), 2843 (3.52  $\mu$ ), 1438 (6.95  $\mu$ ), and 1055 (9.48  $\mu$ ); weak bands at 1327 (7.54  $\mu$ ), 1303 (7.67  $\mu$ ), 950 (10.53  $\mu$ ), and 880 (11.36  $\mu$ ). The ultraviolet spectrum, taken with a Cary Model 11 spectrophotometer over the region 205–700 m $\mu$ , showed no band with an absorbance (optical density) as high as 0.01 for a 4.34  $\times 10^{-3}$  molar solution of tetracyclohexane in spectroqually cyclohexane.

**Dehydrogenation of Tetracyclohexylmethane.**—Into a 50-ml. test tube were placed 0.5 g. of tetracyclohexylmethane, 0.1 g. of 10% palladium on charcoal, and 1 ml. of octadecane as solvent. The top of the test tube was drawn to a capillary and the tube was then immersed in a refluxing bath of diphenyl ether (259°) for 8 hr. The mixture was extracted in a Soxhlet extractor with cyclohexane for 4 hr. and the solvent was then removed. Extensive fragmenting occurred during the high-temperature reaction period and repeated recrystallizations from common hydrocarbon and chlorohydrocarbon solvents failed to separate the components of these mixtures. However, small amounts of tetraphenylmethane were detected by gas chromatographic analysis of these mixtures at 175° on a 100 ft.  $\times$  0.01 in. capillary column coated with DC-550 silicone fluid. An authentic sample of tetraphenylmethane was used to make the chromatographic peak assignment for tetraphenylmethane in the mixture.

### The Facile Rearrangement of Vinyl 3-(Penta-1,4-dienyl) Ether

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In connection with other work in this laboratory, the need for vinyl 3-(penta-1,4-dienyl) ether arose for use as an intermediate in the synthesis program. One of the most attractive routes to this vinyl ether was the vinyl interchange reaction between a vinyl alkyl ether and the appropriate alcohol, which has been found to be of general utility by Watanabe and Conlon<sup>2</sup> and used to a considerable extent by Burgstahler.<sup>3</sup> In this study divinylcarbinol (I) was treated with vinyl alkyl ethers under conditions of the vinyl interchange reaction in an effort to prepare vinyl 3-(penta-1,4-dienyl) ether.

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