

this fraction gave about the same yields of formaldehyde and acetone as were obtained from VII and IX.

**Dimer, C<sub>26</sub>H<sub>46</sub>.**—A higher boiling fraction from the pyrolysis of III proved to be a dimer; b.p. 168–173° (0.65 mm.); *n*<sub>D</sub><sup>20</sup> 1.5201; *d*<sub>4</sub><sup>20</sup> 0.9008; mol. wt. calcd. 352, found 329; yield 3.5%.

*Anal.* Calcd. for C<sub>26</sub>H<sub>46</sub>: C, 88.56; H, 11.44. Found: C, 88.42; H, 11.36.

While an ultraviolet band at 241 mμ (ε 14,360) was consistent with the presence of one highly substituted acyclic conjugated system, other spectroscopic and chemical data provided little definitive information as to the structure of the dimer.

**Thermal Dehydration of *cis*-6,10-Dimethyl-1,5,9-undecatrien-4-ol (IV).**—The apparatus, procedure, and work-up were identical with those used for pyrolysis of III, except that the heating period was 3 hr. instead of 6 hr. Fractional distillation showed that 68% of the products were monomers. Through distillation and gas chromatography, the same four C<sub>13</sub>H<sub>26</sub> isomers were found: VI (59%), VIII (11.7%), IX (26.3%), and X (2%). These compounds were identified by the methods described above.

**Dehydration of *trans*-6,10-Dimethyl-1,5,9-undecatrien-4-ol (III) with Anhydrous Oxalic Acid.**—A solution of III (8 g., 0.04 mole) in 80 ml. of benzene was refluxed over 3.6 g. (0.04 mole) of anhydrous oxalic acid for 1.5 hr. After removal of the oxalic acid, the yellow solution was washed with three 10-ml. portions of water and dried over anhydrous sodium sulfate. Distillation and gas chromatography showed that 94% of the products consisted of a mixture of C<sub>13</sub>H<sub>26</sub> isomers. These were identified as VII (41.3%), VIII (16.3%), IX (29%), and X (13%) by the methods described earlier.

**6,10-Dimethyl-1-*trans*-3-*trans*-5,9-undecatetraene (X).**—Owing to the relatively large amount of X formed in the oxalic acid dehydration, it was possible to collect pure samples from the effluent gas of the chromatograph for spectroscopic studies.

Important infrared bands (in CCl<sub>4</sub>, cm.<sup>-1</sup>) in X occurred at 3087 (w, vinyl =C-H), 1665 (w, R<sub>2</sub>C=CHR), 1632 (w), 1615 (m) and 1573 (w, C=C=C=C=C), 997 (s, vinyl =CH), 941 (s, *trans*-CH=CH), and 890 (s, vinyl =CH<sub>2</sub>). Major ultraviolet

bands occurred at 263 mμ (ε 53,000), 272 mμ (ε 62,900), and 281 mμ (ε 53,600).

**6,10-Dimethylundecane (XI).**—Each of the C<sub>13</sub>H<sub>26</sub> isomers (VII–X) was separated by preparative-scale gas chromatography and individually subjected to catalytic hydrogenation as described under VI. The same, single product was obtained in each case, and was identified as 6,10-dimethylundecane (XI). After purification by vacuum distillation at 4.0–4.5 mm. and preparative-scale gas chromatography (Carbowax 4000 column), XI gave b.p. (micro) 219.0°, *n*<sub>D</sub><sup>20</sup> 1.42435.

*Anal.* Calcd. for C<sub>13</sub>H<sub>26</sub>: C, 84.69; H, 15.31. Found: C, 84.52; H, 14.96.

Key infrared bands (cm.<sup>-1</sup>) for paraffin XI were 1460 (s, —CH<sub>2</sub>—), doublet 1377 and 1370 (s) and 1360 (s) (*gem*-dimethyl), and doublet 715 and 725 (w, —(CH<sub>2</sub>)<sub>4</sub>—). In the n.m.r. spectrum, the twelve CH<sub>3</sub>— protons showed signals at τ 9.18, 9.12, and 9.08; the remaining sixteen protons appeared as an intense doublet centered at τ 8.76 (*J* = 1.2 c.p.s., —CH<sub>2</sub>— in *acyclic* hydrocarbon) and a tail sloping toward 8.2 (H-C<) protons). The entire mass-spectroscopic fragmentation pattern of XI clearly defined its skeletal arrangement.<sup>28</sup> The expected intensity maximum in the low-mass region was observed, with a base peak of *m/e* = 57 (100%). A molecular ion peak (M<sup>+</sup>) appeared at *m/e* = 184 (1.04%). A relatively large peak at *m/e* = 169 (M-15, 1.30%) attested to the easy loss of a methyl group. The position of the internal 6-methyl group was confirmed by the appearance of intense fragments at *m/e* = 113 (8.71%, C<sub>8</sub>H<sub>17</sub><sup>+</sup>) and *m/e* = 99 (4.89%, C<sub>7</sub>H<sub>15</sub><sup>+</sup>).

**Acknowledgment.**—The authors are indebted to Mr. J. B. Bendoraitis and Mrs. B. L. Brown of Socony Mobil Oil Company, Paulsboro, New Jersey, for running the mass spectra and for considerable aid in their interpretation.

(28) See K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 72, and references therein.

## Reaction of Cyclohexene with a "Thermal Dichlorocarbene" from Chloroform

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The pyrolysis of chloroform in the presence of cyclohexene has produced the new compound, 3-dichloromethylcyclohexene, and its structural isomers. Dichloronorcarane and its pyrolysis product, toluene, were also formed. The formation of dichloronorcarane and toluene gives evidence that dichlorocarbene was formed by the pyrolysis of chloroform. The formation of 3-dichloromethylcyclohexene is explained by an insertion reaction of dichlorocarbene with cyclohexene. The major insertion product was identified by comprehensive structural studies.

Besides addition to the double bond of an olefin, Doering<sup>1,2</sup> showed that direct insertion reactions occurred with a highly activated methylene derived from the photolysis of diazomethane. Doering proved that a stepwise process involving free intermediates which can equilibrate and give mixed products was not the method of reaction. Instead, a concerted mechanism for the direct insertion was clearly illustrated.

Unlike methylene, the reaction of dichlorocarbene with olefin has only recently been found to give an insertion reaction. Usually dichlorocarbene<sup>3</sup> has been generated at room temperature or below, by the attack of a base on a haloform, or from an alkoxide on hexachloroacetone or trichloroacetate esters, or from a metal alkyl on a tetrahalomethane. A process involving slightly elevated temperatures is the "ther-

mal" decomposition of salts of trichloroacetic acid at about 100°. Fields<sup>4</sup> suggested that the dichlorocarbene formed by this method has a higher energy level and undergoes reactions not observed with dichlorocarbene produced at low temperatures. Evidence is presented that a dichlorocarbene produced from such a sodium trichloroacetate decomposition reacts with cumene at the benzylic carbon-hydrogen bond to give a 33% yield of insertion product, whereas yields were only 0.5–5% with a low-temperature dichlorocarbene process.

Parham<sup>5</sup> emphasized the importance of the structure of the olefin upon the course of the reaction with his observation that dichlorocarbene underwent, solely, insertion reactions with 2H-1-benzothiopyran and the expected addition to the double bond was not found. On the other hand, no insertion reaction occurred with the isomeric 4H-1-benzothiopyran, and only addi-

(1) W. von E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, *J. Am. Chem. Soc.*, **78**, 3224 (1956).

(2) W. von E. Doering and H. Prinzbach, *Tetrahedron*, **6**, 24 (1959).

(3) W. Kirmse, *Angew. Chem.*, **73**, 161 (1961).

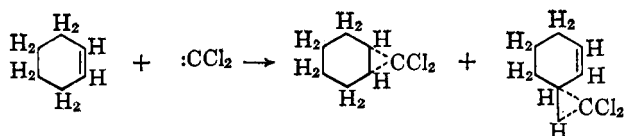
(4) E. K. Fields, *J. Am. Chem. Soc.*, **84**, 1745 (1962).

(5) W. E. Parham and R. Koncos, *ibid.*, **83**, 4034 (1961).

tion to the double bond took place. Parham employed an ionic mechanism for these reactions and showed that a common intermediate ion from both compounds did not exist.

Previous workers<sup>6,7</sup> have postulated the existence of dichlorocarbene as an intermediate in the pyrolysis of chloroform at 450–600°, but capturing agents were not present, and the final product was tetrachloroethylene. Also, in the pyrolysis of difluorochloromethane, difluorocarbene is postulated as an intermediate, which dimerizes to tetrafluoroethylene.<sup>8</sup> This difluorocarbene has also been captured by tetrafluoroethylene to produce a hexafluoropropene.<sup>9</sup>

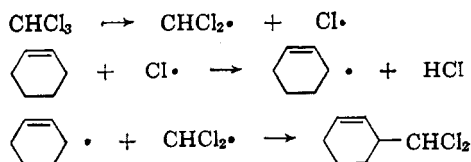
In this study, the thermal reaction of chloroform with cyclohexene has been investigated. We propose that dichlorocarbene is formed from the chloroform and is the active intermediate. Preliminary information on this reaction appeared in a recently issued patent.<sup>10</sup> Besides the addition of this carbene to the double bond of cyclohexene, we have also found that simultaneously a unique C–H insertion reaction takes place with cyclohexene, as illustrated below.



This dichlorocarbene mechanism is supported by the formation of appreciable amounts of toluene as another reaction product. Winberg<sup>11</sup> has shown that the adduct of cyclohexene and dichlorocarbene, dichloronorcarane, forms toluene on pyrolysis.

The dichlorocarbene produced in our study *via* the pyrolysis of chloroform at 500–600° would have a still higher thermal energy than that produced at 100° by Fields.<sup>4</sup> This probably accounts for the different results obtained with cyclohexene in the current study, in comparison with the earlier work by Doering,<sup>12</sup> who obtained a 59% yield of the addition product, dichloronorcarane, without finding an insertion reaction. The possibility that dichloromethylcyclohexene was formed by thermal isomerization of dichloronorcarane was excluded when dichloromethylcyclohexene was not formed by pyrolysis of dichloronorcarane.

An alternate mechanism to the formation of dichloromethylcyclohexene has been proposed by one of the referees as follows.



(6) G. P. Semeluk and R. B. Bernstein, *J. Am. Chem. Soc.*, **79**, 46 (1957).

(7) A. E. Shilov and R. D. Sabirova, *Proc. Acad. Sci. USSR*, **114**, 413 (1957).

(8) F. B. Downing, A. F. Benning, and R. C. McHarness, U. S. Patent 2,551,573 (1951).

(9) L. A. Errede and W. R. Peterson, U. S. Patent 2,979,539 (1961).

(10) F. Strain and P. D. Bartlett (to Pittsburgh Plate Glass Co.), Belgian Patent 610,733 (Nov. 24, 1961); U. S. application, Dec. 9, 1960.

(11) H. E. Winberg, *J. Org. Chem.*, **24**, 264 (1959).

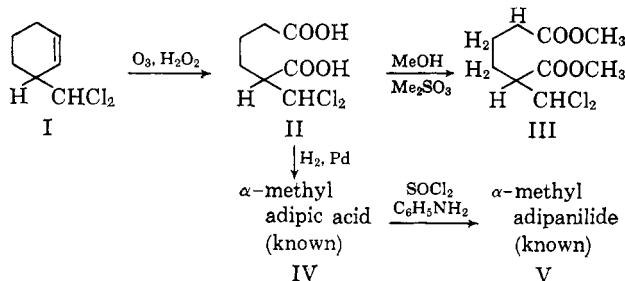
(12) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

Various pyrolytic methods of generating the dichlorocarbene were investigated in our study, but the preferred method employed a suspended, hot platinum wire in the refluxing vapors of the chloroform and cyclohexene. In this way, the olefin was present in high concentrations at the moment of carbene formation. This favors cycloaddition (and insertion in this case) in preference to simple combination of the carbene with the formation of tetrachloroethylene. For example, the pyrolysis of chloroform in the absence of an electron donor produced, in addition to tetrachloroethylene, some pentachloroethane and sizeable amounts of hexachloroethane. With cyclohexene present, the reaction was changed markedly, as no chlorinated ethanes or ethylenes were found.

The exact temperature of the platinum wire used for pyrolysis was not accurately determined. At the start of each experiment, the clean wire was at a dull red heat, but gradually carbon deposited on the wire and an arbitrarily increased voltage was used to compensate for the insulation caused by the carbon.

Very small yields of dichloronorcarane were isolated, due undoubtedly to its decomposition to toluene, which was found in sizeable amounts. The toluene and the new insertion product were obtained in fairly comparable yields of 9–12%, respectively, based on the chloroform reacted, and 12–16% based on the cyclohexene.

The following series of reactions was used to show that the insertion product contained the isomer, 3-dichloromethylcyclohexene.



The identity of  $\alpha$ -dichloromethyladipic acid (II) was confirmed by converting it to methyl  $\alpha$ -dichloromethyladipate (III), and  $\alpha$ -methyladipic acid (IV) whose structures were established by n.m.r. spectra. In addition, the melting point of compound IV and its anilide V corresponded to the values in the literature.<sup>13</sup>

It was shown by degradation studies that the isolated insertion reaction product contained a large amount of 3-dichloromethylcyclohexene, but the n.m.r. spectrum of the fraction purified by preparative g.l.c. did not correspond to 100% purity.

The infrared spectrum of the fraction purified by preparative g.l.c. was correlated with the published spectra<sup>14</sup> of isomeric methylcyclohexenes. It was concluded that at least 90% of the insertion had occurred at the alkyl and the allyl position, and less than 5% had occurred at the vinyl position.

The inability to separate the isomers of dichloromethylcyclohexene by preparative g.l.c. corresponds to Doering's inability to separate the isomers of methylcyclohexene by g.l.c.<sup>1</sup>

(13) E. H. Hansche, *Ber.*, **88**, 1648 (1955).

(14) American Petroleum Institute Research Project 44; National Bureau of Standards, Washington, D. C., 1949.

### Experimental

**Apparatus.**—A 1-l. flask, electrically heated by a mantle, was attached by a 35–45  $\frac{1}{2}$  joint to a 4.5  $\times$  45 cm. vertical Pyrex reactor tube. A water-cooled reflux condenser was attached to the top of the tube reactor by a similar joint. A platinum wire (60 cm.  $\times$  0.025 in.) had been sealed in the reactor tube so that it was suspended in a U-form. A rubber tube lead from the reflux condenser to a 1-l. trap immersed in Dry Ice–acetone. Another tube connected this trap to a second trap partly filled with water.

**Procedure.**—A mixture of 246 g. (3.0 moles) of purified cyclohexene and 359 g. (3.0 moles) of purified chloroform was refluxed vigorously in the 1-l. flask. Then the platinum wire was heated electrically by a Variac for 5 hr. while continuing refluxing. The voltage was 12 at the start and 14 at the end of the experiment. After the heating period, the Dry Ice bath was removed and the trap contents were allowed to warm to room temperature. Finally the trap was heated to slight boiling. Titration of the water trap showed 87 g. (2.46 moles) of hydrogen chloride present.

The product remaining in the original 1-l. flask was combined with the product remaining in the Dry Ice trap. The total weight was 486 g.

**Isolation.**—The combined product was distilled through a 1.7  $\times$  20 cm. Fenske column. The high-boiling products were redistilled several times using a capillary stream of air for smooth boiling and a Dry Ice cooled trap.

The significant fractions obtained are shown in Table I.

TABLE I

Fraction	Weight, g.	B.p., °C.	mm.	$n_D^{20}$
1	395	Dry Ice trap	730–28	...
2	4.0	97–99.5	28	1.521
3	16.5	99.5–102	28	1.5135
4	5.6	102.5–118	28	1.5205

*Anal.* of fraction 3. Calcd. for  $C_7H_{10}Cl_2$ : C, 50.93; H, 6.11; Cl, 42.96. Found: C, 52.45; H, 5.57; Cl, 40.88.

**G.l.c. Analysis.**—The g.l.c. analysis of the low-boiling fraction 1 is shown in Table II. The major unknown impurities are included.

TABLE II

Compd.	Moles, %	Total moles present
Chloroform	41.8	1.67
Cyclohexene	49.1	1.97
Toluene	4.0	0.16
Unknown 1	2.5	...
Unknown 2	1.0	...
Unknown 3	0.8	...
Unknown 4	0.4	...
Unknown 5	0.3	...

Table III shows the g.l.c. analysis in mole per cent of the significant high-boiling fractions with the major unknown impurities included.

TABLE III

Compd.	Fraction		
	2	3	4
Unknown 1	4.7	0.8	9.7
Unknown 2	12.0	...	...
Dichloronorcarane	14.4	4.4	0.8
Dichloromethylcyclohexenes	57.5	88.4	64.9
Unknown 3	3.3	4.0	3.2
Unknown 4	0.2	0.5	4.7
Unknown 5	...	0.1	4.3
Unknown 6	...	...	6.2
Unknown 7	...	...	3.9

Calculations show that 0.01 mole of dichloronorcarane and 0.12 mole of dichloromethylcyclohexene were present in these three fractions.

**Further Purification of Fraction 3 by Preparative Chromatography.**—Fraction 3 was further purified by preparative g.l.c. on a

polar column at 145–150° in 0.25-ml. batches. The main fraction was 99.6% pure dichloromethylcyclohexene according to g.l.c. analysis. It had  $n_D^{20}$  1.5073.

*Anal.* Calcd. for  $C_7H_{10}Cl_2$ : C, 50.93; H, 6.11; Cl, 42.96. Found: C, 51.67; H, 6.08; Cl, 40.94.

**N.m.r. Spectra of Dichloromethylcyclohexene.**—The n.m.r. spectrum of the chromatographically purified dichloromethylcyclohexene showed features that could be attributed to 3-dichloromethylcyclohexene, but the presence of other compounds was also indicated.

**Infrared Spectrum of Dichloromethylcyclohexene.**—Using a Perkin-Elmer Model 521 spectrophotometer, an infrared spectrum was made of the dichloromethylcyclohexene purified by preparative g.l.c.

On the basis of data for the isomeric methylcyclohexenes taken from the literature<sup>14</sup> and making allowance for chlorine, calculations were made for the spectra to be expected for the isomers of dichloromethylcyclohexene. The spectrum found was in agreement with the calculated spectrum for a mixture with the predominant isomer being 3-dichloromethylcyclohexene.

**Material Balance.**—The difference between the amount of starting material and recovered material showed that 1.33 moles of chloroform and 1.03 moles of cyclohexene were converted to other products. The principal products formed were 2.46 moles of hydrogen chloride, 0.16 mole of toluene, 0.12 mole of dichloromethylcyclohexene, and 0.01 mole of dichloronorcarane. The total yield of the last three compounds was 22% based on chloroform and 29% based on cyclohexene.

**$\alpha$ -Dichloromethyladipic Acid by Ozonolysis of Fraction 3.**—

Two grams of fraction 3 and 20 ml. of 90% formic acid were placed, and extremely well-stirred in a reactor immersed in an ice bath. Ozone was passed into the reactor for 5 min. after it was no longer absorbed. Two milliliters of 35% hydrogen peroxide was added and the single liquid phase was kept at about 25° by cooling for several hours. It was then allowed to stand for 4 days at room temperature. The solution was pumped at room temperature and 1 mm. until dry, leaving 2.3 g. of slightly colored solid, which was crystallized from 5 ml. of hot ethylene dichloride. The solid was sublimed at 0.01- $\mu$  pressure, dissolved in hot ethylene dichloride (5 ml.), filtered, and cooled to 0°. The solid was collected by filtration and air-dried. The yield was 1.2 g. (49%), m.p. 116.5–117.5°.

*Anal.* Calcd. for  $C_7H_{10}Cl_2O_4$ : C, 36.70; H, 4.40; Cl, 30.96; equiv. wt., 114.5. Found: C, 36.89; H, 4.22; Cl, 30.71; equiv. wt. (potentiometric titration), 112.5, 115.

In an experiment with a known ozone flow rate, the ozone absorbed by fraction 3 corresponded closely to the calculated value for dichloromethylcyclohexene. Dichloronorcarane did not absorb ozone.

**$\alpha$ -Methyladipic Acid by Hydrogenation of  $\alpha$ -Dichloromethyladipic Acid.**—A 30-ml. Carius tube was charged with 0.2 g. of potassium carbonate, 0.2 g. of 5% palladium on carbon, 0.245 g. (0.00107 mole) of  $\alpha$ -dichloromethyladipic acid, and 5 ml. of acetic acid. The tube was cooled by liquid nitrogen, evacuated, filled with 95 ml. of gaseous hydrogen at slightly less than atmospheric pressure, and sealed off. The tube was agitated for 2 days at 25° and 20 hr. at 150°.

The contents were filtered and 0.6 ml. of concentrated hydrochloric acid was added. The mixture was pumped to dryness, boiled with 5 ml. of ethyl acetate, and filtered. The filtrate was dried at 1 mm. and room temperature. The residue was refluxed with 1.5 ml. of thionyl chloride while excluding moisture. The excess thionyl chloride was removed and the residue was distilled at 1 mm. The distillate was boiled for 10 min. in a test tube with a few milliliters of water and pumped at 1 mm. until most of the water was removed. It was allowed to stand open on its side overnight and pumped again. A 71% yield (0.122 g., m.p. 54–56°) of colorless  $\alpha$ -methyladipic acid was obtained (lit.<sup>15</sup> m.p. 59–60°). The infrared spectra were consistent with this structure.

*Anal.* Calcd. for  $C_7H_{12}O_4$ : C, 52.5; H, 7.6; neut. equiv., 80. Found: C, 51.96; H, 7.33; neut. equiv., 85.

**N.m.r. Spectra of  $\alpha$ -Methyladipic Acid.**—The spectra were obtained on a 60-Mc. Varian HR-60 instrument in deuterated methanol. The chemical shifts compared with tetramethylsilane were methyl,  $\tau$  8.83, doublet, weight 3;  $\beta$ - and  $\gamma$ -hydrogen,  $\tau$  8.41, complex multiplet, weight 4;  $\alpha$ - and  $\delta$ -hydrogen,  $\tau$  7.68, complex multiplet, weight 3; and carboxyl and hydroxyl hydrogen,  $\tau$  5.00, singlet, weight 2+.

**$\alpha$ -Methyladipamide from  $\alpha$ -Methyladipic Acid.**—While excluding moisture with a nitrogen blanket, 0.102 g. of  $\alpha$ -methyladipic acid was refluxed 1 hr. with 1 ml. of thionyl chloride and the excess was removed at 1 mm. at room temperature. The residue was cooled in Dry Ice, 1 ml. of purified aniline was added, and the mixture was shaken and gradually heated, finally for 30 min. at 120°. The reaction product was stirred with boiling dilute hydrochloric acid, cooled, filtered, washed with water, and air dried. Crude  $\alpha$ -methyladipamide<sup>13</sup> was obtained in 74% yield, 0.147 g., m.p. 168–171° (lit.<sup>13</sup> m.p. 172°). Crystallization from 20 ml. of boiling toluene yielded 0.107 g., m.p. 173.5–174.5°.

*Anal.* Calcd. for C<sub>19</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>: C, 73.5; H, 7.14; N, 9.03. Found: C, 73.52; H, 6.80; N, 9.36.

**Preparation of Methyl  $\alpha$ -Dichloromethyladipate.**—A mixture of 0.5 g. of  $\alpha$ -dichloromethyladipic acid, 0.1 g. of *p*-toluenesulfonic acid, 2 ml. of methanol, and 2 ml. of methyl sulfite in a loosely stoppered test tube partly immersed in a bath at 93° was heated for 20 hr. Volatile products were removed at 1 mm. and 120° bath temperature. Then, at 0.01- $\mu$  pressure and 65° bath temperature, a colorless oil was distilled. It weighed 0.5 g. (88%).

*Anal.* Calcd. for C<sub>9</sub>H<sub>14</sub>Cl<sub>2</sub>O<sub>4</sub>: C, 42.04; H, 5.49; Cl, 27.58. Found: C, 43.1; H, 5.74; Cl, 25.08.

**N.m.r. Spectra of Dimethyl  $\alpha$ -Dichloromethyladipate.**—The spectra were made on a 60-Mc. Varian HR-60 instrument in carbon tetrachloride. The chemical shifts with tetramethylsilane as standard were  $\alpha$ -dichloromethyl,  $\tau$  4.28, a doublet, weight 1; methyl,  $\tau$  6.37, singlet,  $\tau$  6.48, singlet, weight 6;  $\alpha$ -hydrogen,  $\tau$ ,

7.10, sextuplet, weight 1;  $\delta$ -hydrogen,  $\tau$  7.80, triplet, weight 2; and  $\beta$ - and  $\gamma$ -hydrogen,  $\tau$  8.30, complex multiplet, weight 4.

**Pyrolysis of Dichloronorcarane.**—In 2 min., 2 ml. of dichloronorcarane<sup>12</sup> was passed through a 1.6-cm.-diameter tube in a 24-in. furnace at 510°. From g.l.c. analysis, it was seen that the 1 g. of condensate contained 48.7% of toluene but no dichloronorcarane or dichloromethylcyclohexene.

In 45 sec., 2 ml. of dichloronorcarane was passed through a 0.5-cm. diameter tube in a 24-in. furnace at 500°. The 1.6 g. of condensate contained 69.4% of recovered dichloronorcarane, 23.5% of an unknown (likely 1,3,5-cycloheptatriene), 2.8% of toluene, but no dichloromethylcyclohexene.

**Decomposition of Chloroform Alone.**—Chloroform alone (1.25 moles) was pyrolyzed in the above apparatus for 3 hr. with the voltage at 10. Besides the 0.86 mole of hydrogen chloride formed, g.l.c. analysis of the higher boiling fraction showed 0.16 mole of perchloroethylene, 0.037 mole of pentachloroethane, and 0.102 mole of hexachloroethane.

**Acknowledgment.**—The n.m.r. spectra were made and interpreted by Mr. T. F. Page, Jr., Battelle Memorial Institute. Dr. Harry Lott of this laboratory made the infrared spectral measurements and interpretation. Helpful discussions with Dr. P. D. Bartlett of Harvard University are also gratefully acknowledged.

## *gem*-Dimetallic Compounds. Ethane-1,1-diboronic Acid and Ethylenedimercuric Chloride<sup>1</sup>

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Dibutyl vinylboronate was hydroborated with excess diborane in tetrahydrofuran. Treatment with butanol replaced the hydrido functions on boron with butoxy groups. Tetrabutyl ethane-1,1-diboronic acid was obtained together with some of the isomeric ethane-1,2-diboronic acid. Hydrolysis yielded the corresponding boronic acids, which were easily separated by precipitating the relatively insoluble ethane-1,2-diboronic acid from moist tetrahydrofuran with methylene chloride. With a limited amount of diborane, dibutyl vinylboronate yielded a mixture of isomeric tris(dibutoxyborylethyl)boranes. Treatment of tetrabutyl ethane-1,1-diboronic acid with mercuric chloride and aqueous alkali yielded polyethylenedimercury or ethylenedimercuric chloride, depending on the proportions of reactants. Polyethylenedimercury reacted with mercuric chloride in refluxing diglyme to yield ethylenedimercuric chloride, or with iodine to yield ethylene iodide. Treatment of ethane-1,2-diboronic acid with mercuric chloride and alkali yielded ethylene, boric acid, and mercurous chloride.

Organometallic compounds having two metallic atoms bonded to the same carbon atom have not been generally available, although the first compound of this class, methylenedimercuric iodide, was synthesized by the reaction of mercury with methylene iodide in sunlight in 1881.<sup>2</sup> Unlikely appearing syntheses of ethylenedimercuric chloride, ethanetetramercuric chloride, ethanhexamercuric chloride, and related compounds have been claimed,<sup>3</sup> but recent work indicates that the first material was actually methylmercuric chloride and the last may have been methanetrimercuric chloride.<sup>4</sup> Recently reported *gem*-dimetallic compounds include a number of  $\alpha$ -metalloalkylsilicon and *gem*-disilicon compounds,<sup>5</sup> methylenedilithium and methyl-

enemagnesium,<sup>6</sup> some *gem*-bisboranes in solution from the hydroboration of acetylenes,<sup>7,8</sup> and a 1,3,5-triboracyclohexane derivative.<sup>9</sup>

As an extension of our studies of the chemistry of dibutyl vinylboronate,<sup>10</sup> we undertook a study of its hydroboration. At that time no isolation of a *gem*-diboron compound had been reported, but a synthesis of tetrabutyl ethane-1,1-diboronic acid remarkably similar to ours has recently appeared.<sup>11</sup>

**Hydroboration Studies.**—The hydroboration of dibutyl vinylboronate was effected by adding the boronic ester to a solution of diborane in tetrahydrofuran. To convert the initially formed boranes to stable, isolable derivatives, we undertook the replacement of the hydrido functions of boron with butoxy groups.

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(2) J. Sakurai, *J. Chem. Soc.*, **39**, 485 (1881).

(3) K. A. Hoffman and E. Eichwald, *Ber.*, **33**, 1337 (1900); K. A. Hoffman, *ibid.*, 1328.

(4) S. V. Belshinskii and M. Usubakunov, *Izv. Akad. Nauk Kirg. SSR*, **90** (1963). *Chem. Abstr.*, **60**, 539 (1964).

(5) P. D. George, M. Prober, and J. R. Elliot, *Chem. Rev.*, **56**, 1065 (1956).

(6) K. Ziegler, K. Nagel, and M. Patheiger, *Z. anorg. allgem. Chem.*, **282**, 345 (1955).

(7) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 3834 (1961).

(8) P. Binger and R. Köster, *Angew. Chem.*, **74**, 652 (1962).

(9) R. Köster and G. Benedikt, *ibid.*, **75**, 346 (1963).

(10) D. S. Matteson, *J. Am. Chem. Soc.*, **82**, 4228 (1960). The name ethyleneboronic acid once used by *Chemical Abstracts* has been changed to etheneboronic acid. We have now decided to call it vinylboronic acid, a name which seems clearer even though it is not strictly systematic.

(11) B. M. Mikhailov and P. M. Aronovich, *Izv. Akad. Nauk SSSR, Ord. Khim. Nauk*, 1233 (1963).