## Characterization of the Dimethyl-1,2-dimethylenecyclobutanes from the Methylallene Thermal Dimerization

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Thermal dimerization of methylallene has been investigated in a static system at 170° for various lengths of time. On the basis of spectral data and chemical evidence, the structures of all seven dimethyl-1,2-dimethylenecyclobutanes possible from the dimerization are assigned, namely trans- and cis-3,4-dimethyl-1,2-dimethylenecyclobutane (1 and 2), 3-methyl-2-methylene-syn-ethylidenecyclobutane (3), 3-methyl-2-methylene-anti-ethylidenecyclobutane (4), syn, syn-1,2-diethylidenecyclobutane (5), anti, syn-1,2-diethylidenecyclobutane (6), and anti,anti-1,2-diethylidenecyclobutane (7). The relative amounts of compounds 1-7 produced at low conversion are 25:4:37:18:13:3:0.5. As the reaction proceeds, however, the relative amounts of 1, 2, 3, and 4 decrease.

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Allene has long been known to give two dimeric products, 1,2- and 1,3-dimethylenecyclobutane, in a ratio of 85:15 along with various oligomers upon heating.<sup>1</sup> However, none of the latter type of dimer (head to tail) has been reported as being formed in the cases of dimerization of substituted allenes. On the basis of these observations, it has been postulated that combination of two molecules of allene occurs initially between two central carbon atoms to form a relatively stable bisallyl diradical which then collapses to the products.<sup>2</sup> Although the stereochemistry of the substituted allene dimers had long been unknown, recent work on dimerizations of tribromoallene,<sup>3,4</sup> trichloroallene,<sup>5</sup> methylallene,<sup>6</sup> chloroallene,<sup>7</sup> and 1,3-dimethylallene<sup>8</sup> revealed that the major products are those with substituents trans on the cyclobutane ring and syn on the exocyclic double bonds. Interest has also focused on the stereochemistry of dimer products from optically active and racemic chiral allenes.8,9

In view of the close relationship of allene dimerization to the degenerate thermal rearrangement of 1,2dimethylenecyclobutanes,<sup>6,10,11</sup> dimerization of methylallene was studied in hopes of providing additional information on the thermal rearrangements of trans- and cis-3,4-dimethyl-1,2-dimethylenecyclobutane<sup>6</sup> (1 and 2). In this work, the characterization of the seven possible nongeminal dimethyl-1,2-dimethylenecyclobutanes and their distribution from the thermal dimerization of methylallene are recorded.

Dimerization of Methviallene.-Thermal dimerization of methylallene in a flow system has been reported,<sup>12</sup> but no compounds were separated or identified; only the molecular weight, 105.9 (Victor Meyer method), of a fraction boiling from 75 to  $135^{\circ}$  (760 Torr) was obtained. The results of dimerization of methylallene in a static system at 170° for various

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lengths of time are given in Table I. Preparative vpc on dibutyl tetrachlorophthalate (DBTCP) allowed



 $^{a}$  Recovered methylallene, 32%(minimum); dimer, 29%; less volatile material, 8%; nonvolatile material, 31%.

7

46

15

 $\mathbf{2.5}$ 

25

0.6

4

isolation of each peak except 4, which was obtained as a mixture with **3**. Large quantities of pure **4** could be obtained from pyrolysis of 1.6

Structural and Stereochemical Assignments. Spectroscopic Studies.-From the uv of each material, it was clear that all were cisoid, conjugated dienes, and the nmr spectral data (Table II) allowed assignment of the stereochemistry in every case.13 Thus, ring proton resonances in 1 are at higher field than those of 2indicating that 1 had trans dimethyls while 2 had the cis stereochemistry. Secondly, methyl groups syn on the double bonds would be expected to be deshielded by the adjacent double bond and therefore at lower field than the anti methyl groups. The nmr spectra and vpc retention times of both 6 and 7 were identical with those of the two 1,2-diethylidenecyclobutanes obtained from the base-catalyzed isomerization of cis-1,2-divinylcyclobutane.14

Chemical Studies.-Chemical evidence for the assignments was also obtained. Thus, to distinguish between the 3,4-dimethyl compounds, 2 was synthesized by an unambiguous route shown in Scheme I.

Thus compound 2 was synthesized from the sensitized, 2 + 2 photocycloadduct of maleic anhydride and 2-butyne,<sup>15</sup> namely 8, by reduction first with lithium aluminum hydride and then with hydrogen gas in methanol over a platinum catalyst giving, mostly, cis-

(13) For background in interpretation of the relative chemical shifts in these systems, see N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964, pp 47, 88, 89.

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 ${\bf TABLE \ II} \\ {\bf Uv}^a \ {\rm and} \ {\bf Nmr}^b \ {\bf Data} \ {\rm for \ all} \ {\bf C_8H_{12} \ Hydrocarbons \ Reported \ Herein}$ 

| Compd | Uv<br>max  |  |                   |                   |                    |                     |             |
|-------|------------|--|-------------------|-------------------|--------------------|---------------------|-------------|
|       |            | Vinyl H's  | exo-Methylene H's | Ring tertiary H's | Ring secondary H's | Vinyl Me H's        | Ring Me H's |
| 1     | <b>244</b> |  | 5.03 s, 4.64 s    | 2.38 m            |                    |                     | 1.18 d      |
| 2     | 245        |  | 5.03 s, 4.65 s    | 2.97 m            |                    |                     | 1.06 d      |
| 3     | 248        | 5.2 q  | 4.98 s, 4.75 s    | 2.7 m             | 2.7 m, 2.1 m       | 1.78 d              | 1.2 d       |
| 4     | 248        | $5.64 \mathrm{m}$  | 5.0 s, 4.6 s      | $2.8 \mathrm{m}$  | 2.8 m, 2.12 m      | $1.62 \mathrm{d}$   | 1.2 d       |
| 5     | 247        | 4.98 q   |                   |                   | $2.40 \ s$         | 1.77 d              |             |
| 6     | 249        | 5.47 q, 5.0 q  |                   |                   | 2.45 br s          | 1.6, 1.7<br>(2 d's) |             |
| 7     | 252        | 5.33 q   |                   |                   | 2.48 s             | 1.55 d              |             |
| 12    | 216        | 6.32 (dd) 1 H; 5.49 (q) 1 H; 4.7-5.3 (m) 4 H; 1.77 (s) 3 H; 1.70 (d) 3 H |                   |                   |                    |                     |             |

**13** 216 6.33 (dd) 1 H; 5.0 (m) 6 H; 2.23 (q) 2 H; 1.05 (t) 3 H

<sup>a</sup> In isooctane, reported in nanometers. <sup>b</sup> At 100 MHz in carbon tetrachloride reported in parts per million downfield from TMS.

1,2-bis(hydroxymethyl)-cis-3,4-dimethylcyclobutane<sup>15</sup> (9), which was treated with excess tosyl chloride in pyridine, doubly displaced with iodide ion in acetone, and doubly dehydroiodinated with molten potassium hydroxide, according to the method of Dorko.<sup>16</sup> The volatile material was a 1:9 mixture of two compounds identical with the first and second vpc peaks, respectively, from the methylallene dimerization. It was also found that hydrogenation with 10% palladium on carbon as catalyst gave the same mixture.

Large quantities of both 1 and 2 were available by reductive dimerization of diethyl ethylidenemalonate to give *meso-* and *threo-1,1,4,4-tetracarbethoxy-2,3*dimethylbutane<sup>17</sup> (10) (1:1 mixture), which could be cyclized to 1,1,2,2-tetracarbethoxy-3,4-dimethylcyclobutane (11) and decarboxylated to a mixture of 3,4dimethylcyclobutane-1,2-dicarboxylic acids,<sup>17</sup> which, after esterification, were reduced with lithium aluminum hydride and then converted to a nearly 1:1 mixture of 1 and 2 by the elimination sequence described above. Compounds 1 and 2 were identical with the first and second vpc peaks from the methylallene dimerization, respectively.

To distinguish between the two 2-ethylidene-4methyl compounds, **3** was subjected to vapor phase pyrolysis at  $260^{\circ 6}$  and gave nearly quantitatively (90%) a triene, 3-methylene-4-methyl-*trans*-1,4-hexadiene (12). The trans stereochemistry was assigned in analogy to Gil-Av's finding that 3-methylcyclobutene gave

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trans-1,3-pentadiene upon pyrolysis<sup>18a</sup> and Frey's results with the thermolysis of 1,2,3,4-tetramethyl- and 1,4-dimethylcyclobutene.<sup>18b,c</sup> The triene 12 could only arise from 3 by a 1,5-hydrogen shift<sup>19</sup> to give 1-vinyl-2,3-dimethylcyclobutene, which would be expected<sup>18,20</sup> to ring open to 12. On the other hand, the anti ma-



terial 4 underwent substantially slower conversion to 12 under these conditions.<sup>6</sup>

Lastly, to distinguish between 5, 6, and 7, the first two were individually subjected to vapor phase pyrolysis at 260° and each gave clearly a new triene, 2ethyl-3-methylene-1,4-pentadiene (13), also via the 1,5-hydrogen shift; 7 was relatively inert under the reaction conditions.<sup>6</sup>

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## Discussion

Dimer Distributions.—The data of Table I reveal that some chemical fractionation of the dimers occurred during the first 65% of reaction. Thus, as the reaction proceeded, the percentages of 1 and 2 decreased relative to the other materials, as did those of 3 and 4, albeit somewhat less. Nevertheless, there had been relatively little fractionation thus allowing the conclusion that the dimer distribution after 1 hr of reaction reflects the relative energetics of pathways leading to the dimers. After extended reaction periods, chemical fractionation is very possible owing to the difference in reactivity of the various products undergoing secondary reactions in the mixture. It is known that tetramethyl-1,2-dimethylenecyclobutane undergoes polymerization much faster than 1,2-diisopropylidenecyclobutane and 1-isopropylidene-2-methylene-3,3-dimethylcyclobutane in the dimerization of 1,1-dimethylallene.20b,21

A second conclusion is that the dimer distribution reflects the relative thermodynamic stabilities of the various compounds within the first family, namely, 1 and 2, but not in the other two, 3 and 4, or 5, 6, and 7. Inspection of models reveals that nonbonded interactions would render 3 less stable than 4, and 5 should be less stable than 6, which in turn would be less stable than 7. Unfortunately, there is presently no experimental verification of these expectations. Nonetheless, it does appear that the transition states for formation of dimeric product reflect the stability of products only at the developing doubly allylic cyclobutane bond and not at the residual unsaturated linkages. It is not obvious what is responsible for the dimer distribution obtained in the methylallene dimerization, but it is possible that as a result of various twisting motions associated with a concerted, or effectively so,<sup>9</sup> cycloaddition, the sterically most favored orientation of addends at the transition state is drawn inexorably into the highest potential energy well on the energy surface responsible for formation of two of the three families of dimeric products.

## **Experimental Section**

General.--Nuclear magnetic resonance spectra were recorded on Varian A-60 and HA-100 spectrometers. Carbon tetrachloride was used as a solvent with TMS (or chloroform) as an internal lock in frequency sweep mode; chemical shifts are reported as  $\delta$  values in parts per million downfield from TMS. Infrared spectra were obtained with Perkin-Elmer Model 137 and 137G spectrophotometers in the indicated phase. Vapor phase chromatography was performed on Varian Aerograph A90P-3 and Series 1220-2 (capillary) instruments using dibutyl tetrachlorophthalate (DBTCP) as liquid phase. For separation and purification, a 15 ft  $\times$  0.25 in. column with 30% DBTCP on 60-80 Chromosorb W was used and operated at 130°, 40 psi, and 60 ml/min of helium. A 200-ft DBTCP capillary column operated at 90° and 30 psi was used for analysis. Mass spectra were taken on an AEI MS-9 mass spectrometer operating at 70 eV. Melting points were measured with a Thomas-Hoover capillary melting point apparatus without correction.

Dimerization of Methylallene.—Heavy wall 5-ml tubes, which were washed with dilute ammonium hydroxide solution and dried, each containing 450  $\mu$ l of methylallene (99+% by vpc), were evacuated and sealed at liquid nitrogen temperature. Four such tubes were placed in a 150-ml stainless steel bomb, which contained about 10 ml of benzene for balancing the vapor pressure of methylallene at reaction temperature, and heated at  $170^{\circ}$  in an oven for the desired lengths of time. The compositions of the dimers were determined by analyses of the samples taken from several individual tubes on a 200-ft DBTCP capillary column. Retention times were compared with those of authentic samples. The average percentage compositions of the dimers obtained from pyrolyses for 1, 13, and 20 hr are shown in Table I.

The reaction mixture from a 13-hr reaction (5.78 g) was fractionated bulb to bulb, giving 1.83 g (31.6%) of unchanged methylallene, from 760 to 135 Torr at room temperature, 1.66 g (28.8%) of a dimer fraction from 10 to 0.5 Torr at room temperature, 0.5 g (8.65%) of a liquid at 0.5 Torr at 95°, and 1.79 g (31%) of a residue. After passage of 1.5 g of the distilled dimer mixture through a preparative DBTCP column, the following compounds, 1-7, in the order of increasing retention time were obtained.

trans-3,4-Dimethyl-1,2-dimethylenecyclobutane (1).—Nmr and ir spectra were superimposable in all respects on those of the pure compound obtained by independent synthesis (see below).

cis-3,4-Dimethyl-1,2-dimethylenecyclobutane (2).—Nmr and ir spectra were superimposable in all respects on those of the pure compound obtained by independent synthesis (see below).

3-Methyl-2-methylene-syn-ethylidenecyclobutane (3).—3-Methyl-2-methylene-syn-ethylidenecyclobutane (3) was obtained pure by passage three times through the DBTCP preparative column: nmr (CCl<sub>4</sub>, 100 MHz)  $\delta$  1.2 (d, J = 6 Hz, 3 H), 1.78 (d with fine structure, J = 6 Hz, 3 H), 2.1 (m, 1 H), 2.7 (m, 2 H), 4.75 (s, 1 H), 4.98 (s, 1 H), 5.2 (q with fine structure, 1 H); ir (CCl<sub>4</sub>) 3.24 (w), 3.3 (sh), 3.38 (s), 3.42 (s), 3.48 (m), 6.0 (m), 6.14 (m), 6.92 (m), 7.31 (m), 11.43  $\mu$  (s); uv (isooctane) 239, 248 ( $\lambda_{max}$ ), 258 nm; m/e 108.0946 (calcd for C<sub>8</sub>H<sub>12</sub>, 108.0939).

**3-Methyl-2-methylene**-anti-ethylidenecyclobutane (4).—3-Methyl-2-methylene-anti-ethylidenecyclobutane (4) was not obtained pure from the dimer mixture, since even with repeated injections through the column it was still contaminated by **3**. However, it could be isolated from the pyrolysate of the stereospecific thermal rearrangement of **1** (see below).

syn,syn-1,2-Diethylidenecyclobutane (5): nmr (CCl<sub>4</sub>, 100 MHz)  $\delta$  1.77 (d, J = 7 Hz, 6 H), 2.4 (s with fine structure, 4 H), 4.98 (q, J = 7 Hz, 2 H); ir (CCl<sub>4</sub>) 3.3 (sh), 3.37 (s), 3.42 (s), 3.49 (m), 4.28 (w), 6.94 (m), 6.99 (m), 7.26 (sh), 7.32 (m), 9.54 (w), 9.77 (w), 10.73  $\mu$  (m); uv (isooctane)  $\lambda_{\text{max}}$  247 nm; m/e 108.0946.

anti,syn-1,2-Diethylidenecyclobutane (6): nmr (CCl<sub>4</sub>, 100 MHz)  $\delta$  1.6, 1.7 (2 overlapped d's, J = 7 Hz, 6 H), 2.45 (broad s, 4 H), 5.0 (q with fine structure, J = 7 Hz, 1 H), 5.47 (q with fine structure, J = 7 Hz, 1 H); ir (CCl<sub>4</sub>) 3.3 (m), 3.38 (s), 3.4 (s), 3.49 (m), 3.52 (sh), 4.28 (w), 6.06 (w), 6.98 (m), 7.08 (sh), 7.3 (m), 10.35 (w), 10.7 (w), 12.08  $\mu$  (s); uv (isooctane) 241, 249 ( $\lambda_{max}$ ), 250 nm; m/e 108.0946.

anti, anti-1, 2-Diethylidenecyclobutane (7).—This compound was isolated after repeated injections: nmr (CCl<sub>4</sub>, 100 MHz)  $\delta$  1.55 (d, J = 7 Hz, 6 H), 2.48 (s, 4 H), 5.33 (q with fine structure, J = 7 Hz, 2 H); ir (CCl<sub>4</sub>) 3.3 (w), 3.37 (m), 3.4 (m), 3.42 (m), 3.5 (w), 6.04 (w), 6.94 (m), 7.3  $\mu$  (w); uv (isooctane) 243, 252 ( $\lambda_{max}$ ), 262 nm; m/e 108.0937.

cis-3,4-Dimethyl-1,2-dimethylenecyclobutane (2).—To a cold solution of 8 g (42 mmol) of recrystallized p-toluenesulfonyl chloride in 20 ml of pyridine was added a cold solution of 2 g (13.9 mmol) of crude cis-1,2-bis(hydroxymethyl)-cis-3,4-dimethylcyclobutane<sup>15</sup> (9) in 10 ml of pyridine and the solution was stirred for 3 hr at 0°. Then to the reaction mixture was added a small volume of ice water. After the mixture was stirred for 20 min, it was poured into ice water. The solid precipitate was filtered from the mixture and dissolved in ether. This ether solution was dried over anhydrous magnesium sulfate and evaporated *in vacuo*, giving 4.4 g (70% yield) of white crystals. Recrystallization from ether-pentane gave cis-3,4-dimethyl-cis-1,2-bis(tosyloxymethyl)cyclobutane: mp 102-103°; nmr (CD-Cl<sub>3</sub>, 60 MHz)  $\delta$  0.9 (m, width at half-height 8 Hz, 6 H), 1.9-2.8 (complex m, 4 H), 2.43 (s, 6 H), 4.05 (m, width at halfheight 8 Hz, 4 H), 7.54 (A<sub>2</sub>B<sub>2</sub>, J = 8 Hz, 8 H); ir (CS<sub>2</sub>) 3.36 (sh), 3.46 (m), 7.32 (s), 8.4 (sh), 8.5  $\mu$  (s).

To a boiling solution of 6.2 g (41.3 mmol) of sodium iodide in 50 ml of acetone was added a solution of 4.4 g (9.75 mmol) of the ditosylate in 45 ml of acetone. After the reaction mixture was refluxed for 33 hr, it was evaporated to dryness, and the residue was dissolved in ether. The yellow ether layer was then washed with a saturated aqueous sodium sulfite solution until the organic

<sup>(21)</sup> S. V. Lebedev, J. Russ. Phys. Chem. Soc., 43, 1735 (1911); Chem. Abstr., 6, 1373 (1912).

The diiodide was added to molten potassium hydroxide under the reaction conditions described by Dorko.<sup>16</sup> A liquid pyrolysate was obtained in 40% yield which was analyzed on a DBTCP capillary column indicating a major peak greater than 90%. The major component was isolated in the pure form by passage of the crude pyrolysate through a preparative DBTCP column: nmr of 2 (CCl<sub>4</sub>, 100 MHz)  $\delta$  1.06 (d, J = 7 Hz, 6 H), 2.97 (complex m, width at half-height 14 Hz, 2 H), 4.65 (s, 2 H), 5.03 (s, with fine structure, 2 H); ir (CCl<sub>4</sub>) 3.32 (m), 3.45 (s), 3.5 (sh), 5.67 (m), 6.07 (m), 6.9 (m), 11.35  $\mu$  (vs); uv (isooctane) 238 (sh), 245 ( $\lambda_{max}$ ), 255 nm (sh); m/e 108.0932 (calcd for C<sub>8</sub>H<sub>12</sub>, 108.0939).

meso- and threo-1,1,4,4-Tetracarbethoxy-2,3-dimethylbutane (10).-A modification of Vogel's method<sup>17</sup> for preparation of meso- and threo-1,1,4,4-tetracarbethoxy-2,3-dimethylbutane (10) was employed. In a 5-1. flask, 40 g of household thin aluminum foil (Kaiser Aluminum and Chemical Corp., Oakland, Calif.) in strips about  $1 \times 3$  in., which were loosely folded, was placed and covered with a 5% aqueous solution of sodium hydroxide for exactly 2.5 min. After decantation of the solution, the foil was washed with water and then with absolute ethanol. Immediately a sufficient quantity of a 2% aqueous solution of mercuric chloride was added to cover the foil completely. After having been allowed to stand for exactly 3 min, the aqueous solution was poured off and the metal was washed with water, then with absolute ethanol, then with moist ether (USP, and a trace of water added), and finally covered with 31. of ether in the presence of an additional 25 ml of water. Immediately to this amalgam was added slowly with stirring 120 g of diethyl ethylidenemalonate.<sup>22</sup> A vigorous reaction took place and continued for 1.5-2 hr. The reaction mixture was stirred further at room temperature overnight and then filtered to remove the aluminum residue and mercury. Evaporation of the ethereal solution residue and mercury. Evaporation of the enterest solution gave 114 g (95% yield) of 10 as a viscous liquid: bp 155-160° (0.5 mm);  $n^{17.0}$  D 1.4480 (lit.<sup>17</sup> 1.44873); nmr (CCl<sub>4</sub>, 60 MHz)  $\delta$  0.85 (d, J = 7 Hz, 3 H), 1.0 (d, J = 7 Hz, 3 H), 1.26 (t with fine structure, J = 7 Hz, 12 H), 2.25 (m, 2 H), 3.25 (unsymmetrical t, 2 H), 4.14 (q with fine structure, J = 7 Hz, 8 H); ir (neat) 3.42 (m), 5.78  $\mu$  (s).

1,1,2,2-Tetracarbethoxy-3,4-dimethylcyclobutane (11).—For preparation of 1,1,2,2-tetracarbethoxy-3,4-dimethylcyclobutane (11), Vogel's method was followed.<sup>17</sup> Distillation of the crude liquid product at 170–180° (0.5 mm) gave a pure colorless oil:  $n^{16.7}$ D 1.4590 (lit.<sup>17</sup> 1.45573, impure); nmr (CCl<sub>4</sub>, 60 MHz)  $\delta$  1.0 (d with fine structure, J = 7 Hz, 6 H), 1.25 (t with fine structure, J = 7 Hz, 12 H), 2.82 (m, 2 H), 4.15 (m, 8 H); ir (neat) 3.44 (m), 5.78  $\mu$  (s).

1,2-Dicarbethoxy-3,4-dimethylcyclobutane (14).—Saponification of 100 g (0.269 mol) of crude 11 in 215 ml of absolute ethanol with 100 g (1.78 mol) of potassium hydroxide in 180 ml of water, followed by acidification with dilute sulfuric acid according to Vogel's method,<sup>17</sup> gave 53 g (76% yield) of the corresponding crude tetraacid: ir (neat) 3.18 (broad, m), 3.4 (m), 5.77  $\mu$  (s). This tetraacid was then decarboxylated under nitrogen to yield 35 g of a gummy residue which was immediately esterified with 900 ml of absolute ethanol in the presence of 10 ml of concentrated sulfuric acid to give 38 g of a dark brown liquid. On fractionation, 34 g (55.5% yield, overall) of pale yellow liquid 1,2-dicarbethoxy-3,4-dimethylcyclobutane (14) was collected at 90– 115° (0.5 mm): nmr (CCl<sub>4</sub>, 60 MHz)  $\delta$  0.83–1.42 (complex m, 12 H), 1.82–2.75 (complex m, 4 H), 3.9–4.35 (complex m, 4 H); ir (neat) 3.44 (m), 5.78  $\mu$  (s).

3,4-Dimethyl-1,2-bis(hydroxymethyl)cyclobutane (15).—To a stirred suspension of 9.8 g (0.258 mol) of lithium aluminum hydride in 400 ml of anhydrous ether at 0° was added, dropwise, a solution of 34 g (0.149 mol) of 14 in 400 ml of anhydrous ether. The reaction mixture was stirred for 9 hr at room temperature, then hydrolyzed with a freshly prepared saturated aqueous solution of anhydrous sodium sulfate, and filtered. The white cake

was washed thoroughly with tetrahydrofuran. The washings and the original filtrate were combined and dried over anhydrous sodium sulfate. Evaporation of the solvents *in vacuo* to 50° gave 20.5 g (95.5% yield) of 3,4-dimethyl-1,2-bis(hydroxymethyl)cyclobutane (15) as a viscous liquid: nmr (CDCl<sub>3</sub>, 60 MHz)  $\delta$  0.94 (m, 6 H), 1.25–3.0 (complex m, 4 H), 3.62 (m, 4 H), 4.5 (broad s, 2 H, concentration-dependent); ir (neat) 3.08 (broad, s), 3.48 (s), 6.89 (m), 7.27 (m), 9.65  $\mu$  (broad, s).

trans-3,4-Dimethyl-1,2-dimethylenecyclobutane (1).—The mixture of diols 15 was converted to the ditosylates, displaced with iodide ion in acetone, and dehydroiodinated in the same manner as described for the preparation of 2 from 9.

Analysis on a 200-ft DBTCP capillary column indicated that the crude reaction product consisted of two major components which accounted for 96% of the mixture, in a ratio of 47 to 53in the order of increasing retention time. The mixture was separated by passage through a preparative DBTCP column into two pure compounds, which were pure by capillary vpc. The compound with longer retention time (on both capillary and preparative columns) had superimposable nmr, ir, uv, and vpc with those of 2 prepared by the sequence described above. The compound with the shorter retention time was assigned as trans-3,4-dimethyl-1,2-dimethylenecyclobutane (1): nmr (CCl<sub>4</sub>, 100 MHz)  $\delta$  1.18 (d, J = 6 Hz, 6 H), 2.38 (complex m, width at half-height 14 Hz, 2 H), 4.64 (s, 2 H), 5.03 (s with fine structure, 2 H); ir (CCl<sub>4</sub>) 3.33 (m), 3.46 (s), 3.52 (sh), 5.69 (m), 6.03 (sh), 6.1 (m), 6.92 (m), 11.35  $\mu$  (vs); uv (isooctane) 238 (sh), 244 ( $\lambda_{max}$ ), 255 nm (sh); m/e 108.0943 (calcd for C<sub>8</sub>H<sub>12</sub>, 108.0939).

Pyrolysis of 1 to 3-Methyl-2-methylene-anti-ethylidenecyclobutane (4).—A well-conditioned 5-1. flask containing 100  $\mu$ l of 1 was sealed at 0.5 mm at liquid nitrogen temperature and heated at 260° for 4 hr. After having been condensed in a liquid nitrogen trap, 85  $\mu$ l of a pyrolysate was obtained. Analysis on a 200-ft capillary DBTCP column indicated the following composition: 35.4% of unchanged 1, 22.2% of 12, 3.32% of 3, 33.2% of 3-methyl-2-methylene-anti-ethylidenecyclobutane (4), and other possible isomers, except 5, in small amounts. Pure 4 was isolated from the pyrolysate by passage through a preparative DBTCP column: nmr (CCl<sub>4</sub>, 100 MHz)  $\delta$  1.2 (d, J = 7Hz, 3 H), 1.62 (d with fine structure, J = 8 Hz, 3 H), 2.12 (complex m, 1 H), 2.8 (complex m, 2 H), 4.6 (s, 1 H), 5.0 (s, 1 H), 5.64 (complex m, 1 H); ir (CCl<sub>4</sub>) 3.24 (w), 3.38 (s), 3.42 (s), 3.48 (m), 5.98 (m), 6.11 (m), 6.92 (m), 7.12 (w), 7.29 (m), 10.45 (m), 11.05 (m), 11.55  $\mu$  (s); uv (isooctane) 240 (sh), 248 ( $\lambda_{max}$ ), 257 nm (sh); m/e 108.0942.

3-Methylene-4-methyl-trans-1,4-hexadiene (12).—Pyrolysis of 40  $\mu$ l of 3 at 260° for 2 hr in a 5-l. bulb, which had been evacuated at 0.5 Torr, gave 30  $\mu$ l of a pyrolysate. Analysis by capillary vpc indicated only one product. After purification on a DBTCP column, the product was assigned as 3-methylene-4-methyl-trans-1,4-hexadiene (12) from the spectral data and the analogous precedents:<sup>18,20</sup> nmr (CCl<sub>4</sub>, 100 MHz)  $\delta$  1.7 (d, J = 7 Hz, 3 H), 1.77 (s, 3 H), 4.91 (overlapped d with fine structure, J = 8 Hz, 3 H), 5.16 (d of d, J = 18, 2 Hz, 1 H), 5.49 (q, J = 7 Hz, 1 H), 6.32 (d of d, J = 18, 10 Hz, 1 H); ir (CCl<sub>4</sub>) 3.23 (m), 3.32 (sh), 3.35 (m), 3.42 (s), 3.48 (m), 6.18 (sh), 6.32 (m), 6.35 (m), 6.96 (m), 7.06 (m), 7.28 (m), 10.07 (vs), 10.9 (vs), 11.2  $\mu$  (vs); uv (isooctane) 216 (Amax), 230 nm (sh); m/e 108.0940.

2-Ethyl-3-methylene-1,4-pentadiene (13).—Similarly, pyrolysis of 120  $\mu$ l of pure 5 at 260° for 2 hr gave 100  $\mu$ l of a liquid pyrolysate which showed complete disappearance of the starting material and three products in the ratio 2:1:1 on analytical vpc. Upon separation and purification by preparative vpc, the latter two were identified as 6 and 7, respectively, and the major product was identified as 2-ethyl-3-methylene-1,4-pentadiene (13) by its spectra: nmr (CCl, 100 MHz)  $\delta$  1.05 (t, J = 7 Hz, 3 H), 2.23 (q, J = 7 Hz, 2 H), 4.97 (m with fine splitting, 5 H), 5.21 (d, J = 18 Hz, 1 H), 6.33 (d of d, J = 18, 10 Hz, 1 H); ir (CCl<sub>4</sub>) 3.25 (m), 3.37 (m), 3.46 (sh), 6.1 (sh), 6.3 (m), 6.9 (m), 7.29 (m), 10.12 (m), 10.95 (s), 11.12  $\mu$  (vs); uv (isooctane) 215.9 ( $\lambda_{max}$ ), 223 nm; m/e 108.0941.

**Registry No.**—1, 26198-76-5; 2, 26198-75-4; 3, 26198-77-6; 4, 26198-78-7; 5, 32414-36-1; 6, 22467-63-6; 7, 22467-62-5; meso-10, 32414-37-2; threo-10, 32414-38-3; 11, 32388-86-6; 12, 26198-74-3; 13, 26111-15-9; 14, 32388-88-8; 15, 32388-89-9; methylallene,

<sup>(22)</sup> W. S. Fones, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 293.

590-19-2; cis-3,4-dimethyl-cis-1,2-bis(tosyloxymethyl)cyclobutane, 32388-90-2; cis-3,4-dimethyl-cis-1,2-bis-(iodomethyl)cyclobutane, 32388-91-3.

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## Dehydration of 3,4-Dimethyl-3,4-hexanediol to the Six Possible C<sub>8</sub>H<sub>14</sub> Dienes and Proof of Structure of the Substituted Butadienes<sup>1</sup>

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3,4-Dimethyl-3,4-hexanediol (1) has been dehydrated, using a variety of reagents, to mixtures of the six isomeric  $C_8H_{14}$  dienes. The use of acidic reagents, or iodine in propionic anhydride, favors the formation of *cis,cis*-3,4-dimethyl-2,4-hexadiene (2) and *cis,trans*-3,4-dimethyl-2,4-hexadiene (3), the dehydration following the Saytzeff pathway. An initial cis double bond is favored over an initial trans configuration because the conformations of the diol leading to a cis double bond exhibit less steric crowding. Phenyl isocyanate as a dehydrating agent is unusual in that double bond formation predominately follows the Hofmann pathway; even 2,3-diethylbutadiene can be prepared in this manner. The structures of the dienes follow from their spectral data. Models show that only the cis, cis isomer of the 3,4-dimethyl-2,4-hexadienes can exist in a conformation with the double bonds coplanar, and only this isomer absorbs strongly in the uv. Infrared and nmr spectra follow a consistent pattern to support the structural assignments. The boiling points of the six isomers range from 104 to 134° (760 mm).

Dehydration of a mixture of meso and dl pinacol 1, 3,4-dimethyl-3,4-hexanediol, prepared from ethyl methyl ketone can give rise to six substituted isomeric butadienes of the formula  $C_8H_{14}$ . The purpose of this work was to prepare and characterize these dienes. Previously, two of the dienes (2 and 3) have been satis-



factorily characterized by Criegee;<sup>2a</sup> the other four are new compounds. Recently, 4 has been reported to be formed in the thermal decomposition of 2-butenylsilver. No yield was given.<sup>2b</sup> The synthesis of  $7^{3.4}$ and of a mixture of 5 and  $6^4$  has been claimed by earlier workers but Criegee<sup>2</sup> has shown the assignments of Gostunskaya, *et al.*, to be in error, and the later synthesis of 7,<sup>3</sup> based on an abnormal Grignard reaction, appears to be doubtful. The isolation was by distillation, the boiling point does not agree with ours, and neither glpc nor nmr spectra were used to characterize the fraction obtained.

Dehydration of 3,4-Dimethyl-3,4-hexanediol.-The dehydration of pinacol, 2,3-dimethyl-2,3-butanediol, has been studied over the past hundred years with a variety of reagents. With pinacol, only two products are possible, 2,3-dimethylbutadiene and pinacolone. It has been observed that pinacolone formation is favored by the use of less strong acids such as phosphoric or oxalic acids, whereas the use of hot strong acids such as hydrobromic acid causes dehydration to the diene to predominate. Iodine<sup>5</sup> and phenyl isocyanate<sup>6</sup> are known to be effective reagents for dehydrating pinacol to butadiene with little pinacolone formation. With 3.4-dimethyl-3.4-hexanediol, dehydration can lead to the two isomeric pinacolones or any of the six isomeric dienes.

We have studied the dehydration of a dl-meso mixture of the 3,4-dimethyl-3,4-hexanediols with a variety of reagents and the results are tabulated in Table I. The pinacol was obtained by the reduction of ethyl methyl ketone with magnesium and was an approximately 1:1 mixture of the dl and meso isomers.

The data in Table I show that iodine in propionic anhydride is the reagent of choice for the preparation of a diene mixture consisting mostly of the cis-cis (2) and cis-trans (3) isomers. The use of iodine alone is somewhat less desirable. Of the six possible isomers, these two are the ones preferentially formed in most of the dehydration reactions. The third most easily formed isomer is 5; this is the major product when phenyl isocyanate is used as the dehydrating agent. This latter reagent is unique in that it preferentially forms a methylene rather than an ethylidene bond. Thus, 7 is also a major product using phenyl isocyanate whereas it is only a minor product in all of the other dehydration reactions. Sulfuric acid and hydrogen bromide also cause isomers 2, 3, and 5 to predominate, and with the latter reagent only small amounts of the pinacolones are formed. The use of potassium acid

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