

bp 74–75° (2 mm)]; infrared (CCl<sub>4</sub>), 3300, 3030, 3010, 1645, 1448, 1432, 1138, 1067, 1049, 1010, 973, 888, 835, 720, 678, and 662 cm<sup>-1</sup>.

**3,4-Tetramethylene-2,3-dihydrofuran (8).**—The major product (56%) from the pyrolysis of **6** displayed the following physical data: infrared (neat), 2910, 2850, 1670, 1470, 1445, 1100, 1085, 1060, 1040, 940, 920, 835, and 788 cm<sup>-1</sup>; uv max (95% ethanol) 214 mμ (ε 6100).

The enol ether **8** (50 mg) was hydrogenated in ethyl acetate with 5% platinum oxide on charcoal to give essentially one compound as shown by vpc analysis. A sample of the saturated ether collected by preparative vpc showed the following physical data: infrared (CCl<sub>4</sub>), 2930, 2860, 2670, 1590, 1480, 1450, 1135, 1082, 1060, 1030, 968, 926, and 892 cm<sup>-1</sup>; δ<sub>TMS</sub><sup>13C</sup> (in ppm) 3.6 (m, 4 H, CHO), 2.2 (broad, 2 H, >CH-), and 1.5 (broad single peak, 8 H, CH<sub>2</sub>). Both infrared and nmr spectra were superimposable with those of *cis*-hexahydrophthalan (**9**).

**cis-Hexahydrophthalan (9).**—Following the procedure of Warnell and Shriner for the ozonolysis of an olefin,<sup>19</sup> bicyclo[4.2.0]oct-7-ene<sup>31</sup> (0.50 g, 0.046 mol) in anhydrous ethanol (40 ml) was cooled in an ice bath and a stream of ozone in oxygen (2%) was passed through the solution for 0.5 hr. The ethanol solution was allowed to warm to room temperature and concentrated *in vacuo*. The crude liquid ozonide was dissolved in ether (5 ml) and added dropwise to a stirred suspension of lithium aluminum hydride (1.0 g) in ether (20 ml). The mixture was allowed to stir for 1 hr then refluxed for 0.5 hr. Excess hydride was quenched with water and 2 *N* hydrochloric acid (1 ml) was added. The solution was allowed to stir until hydrolysis was complete. The ether solution was filtered and dried (Na<sub>2</sub>SO<sub>4</sub>). Removal of the ether *in vacuo* gave 0.50 g of a colorless viscous liquid. A small amount of this liquid was dissolved in ether and induced to crystallize by keeping it in the freezer overnight. The white crystals had mp 40–42° (lit.<sup>37</sup> mp 42–43° for *cis*-hexahydrophthalyl alcohol).

Without further purification, the liquid diol was refluxed with 18% sulfuric acid (2 ml) for 20 min, in a manner similar to that reported<sup>20,21</sup> to give 0.40 g of a liquid with a terpenelike odor which was shown to be essentially one compound by vpc analysis. The infrared spectrum of **9** was identical with that published for *cis*-hexahydrophthalan.<sup>38</sup>

(37) B. T. Gillis and P. E. Beck, *J. Org. Chem.*, **28**, 1388 (1963).

**Bicyclo[3.2.0]heptan-6-one (10).**—Following the procedure of Brown and Zweifel for the hydroboration of an olefin,<sup>39</sup> bicyclo[3.2.0]hept-6-ene<sup>39</sup> (18.2 g, 0.19 mol) yielded 17.0 g of a colorless liquid alcohol. Chromic acid oxidation<sup>40</sup> gave 13.0 g of crude product. Distillation afforded 5.0 g (24%) of colorless liquid: bp 65–70° (16 mm) [lit.<sup>41</sup> bp 162–166°]; infrared (CHCl<sub>3</sub>), 1780 cm<sup>-1</sup>. The semicarbazone derivative had mp 200–201.5° (lit.<sup>41</sup> mp 198.5–201°).

**Bicyclo[4.2.0]octan-7-one (11).**—Following the procedure of Brown and Garg for the conversion of olefins into ketones,<sup>24</sup> 3.0 g (0.028 mol) of bicyclo[4.2.0]oct-7-ene<sup>31</sup> gave 1.2 g (35%) of colorless liquid: bp 55–60° (4 mm) [lit.<sup>9</sup> bp 89–90.5° (25 mm)]; infrared (neat), 1780 cm<sup>-1</sup>.

**Pyrolysis of 10.**—The pyrolysis of 0.40 g of **10** in the manner described above gave a gas and a low-boiling liquid. The liquid was analyzed by vpc on a Perkin-Elmer RX column<sup>28</sup> at 75°. The retention time of the liquid was identical with that of cyclopentene. A sample of the liquid was collected from the gas chromatograph. The infrared spectrum was superimposable with that of authentic cyclopentene.<sup>42</sup>

**Pyrolysis of 11.**—The pyrolysis of 0.25 g of **11** in the manner described above gave a gas and a low-boiling liquid. The liquid was analyzed by vpc on a Perkin-Elmer RX column<sup>28</sup> at 75°. The retention time of the liquid was identical with that of cyclohexene. A sample of the liquid, collected from the gas chromatograph, had an infrared spectrum which was superimposable with that of authentic cyclohexene.<sup>42</sup>

**Registry No.**—**2**, 19656-91-8; **4**, 766-02-9; **4** ( $\alpha$ -naphthylurethane derivative), 19656-93-0; **6**, 285-57-4; **7**, 19656-95-2; **7** (2,4-dinitrophenylhydrazone derivative), 19656-96-3; **8**, 19656-97-4; **9**, 13149-01-4; 2-( $\Delta^2$ -cyclohexenyl)ethanol, 16452-34-9.

**Acknowledgment.**—The author would like to thank Professor O. L. Chapman for valuable discussions.

(38) J. Entel, C. H. Ruof, and H. C. Howard, *J. Amer. Chem. Soc.*, **74**, 441 (1952).

(39) H. C. Brown and G. Zweifel, *ibid.*, **83**, 2544 (1961).

(40) H. C. Brown and C. P. Garg, *ibid.*, **83**, 2952 (1961).

(41) A. T. Blomquist and J. Kwiatek, *ibid.*, **73**, 2098 (1951).

(42) Aldrich Chemical Co., Milwaukee, Wis.

## Diels-Alder Adducts of 1,3-Dimethyl-1,3-cyclohexadiene

R. N. MIRRINGTON AND K. J. SCHMALZL

Department of Organic Chemistry, University of Western Australia, Nedlands, Western Australia 6009

Received October 22, 1968

The structures and stereochemistry of the major Diels-Alder adducts of 1,3-dimethyl-1,3-cyclohexadiene (**2**) with methyl vinyl ketone, methyl acrylate, and ethyl propiolate have been established as **4a**, **4b**, and **6d**, respectively. Lactonization of acid **4c** afforded either novel  $\delta$ -lactone **7** or  $\gamma$ -lactone **8** as the major product depending on the conditions used. Lactone **7**, the kinetically stable product, represents the first of such  $\delta$ -lactones to be isolated in the bicyclo[2.2.2]octane series.

In connection with our work on the total synthesis of novel terpene skeletons, we required a supply of *endo*-1,5-dimethylbicyclo[2.2.2]oct-5-en-2-yl methyl ketone (**4a**). Although a Diels-Alder reaction between 1,3-dimethyl-1,3-cyclohexadiene (**2**) and methyl vinyl ketone would be expected<sup>1</sup> to yield **4a** as the major product, we considered it necessary to make a detailed study of the nature of the adduct(s) from this reaction, particularly since no Diels-Alder adducts of **2** have been described previously, and because the stereochemical and structural integrity of **4a** was vital for our future work.

(1) (a) H. L. Holmes, *Org. Reactions*, **4**, 60 (1948); (b) K. Alder, "Newer Methods of Preparative Organic Chemistry," Vol. 1, Interscience Publishers, New York, N. Y., 1948, p 381.

## Discussion

**1,3-Dimethyl-1,3-cyclohexadiene.**—The Grignard addition of methylmagnesium halide to 3-methyl-2-cyclohexen-1-one has been reported several times<sup>2–6</sup> and, except in two cases,<sup>2,6</sup> the product has been described as 1,3-dimethyl-1,3-cyclohexadiene (**2**). However, von Auwers<sup>2</sup> isolated carbinol **1**, which could be dehydrated to a diene, considered by him to be **3**. On the other hand, Thomas and Stoll<sup>6</sup> demonstrated by

(2) K. von Auwers, *Ber.*, **46**, 2988 (1913).

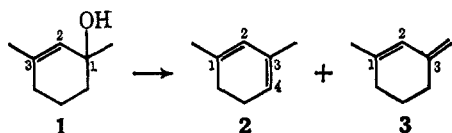
(3) W. N. Haworth, *J. Chem. Soc.*, **103**, 1242 (1913).

(4) A. J. Birch, *ibid.*, 1642 (1947).

(5) (a) R. Y. Levina, N. P. Shusherina, K. D. Gir, and E. G. Treshchova, *Zh. Obshch. Khim.*, **24**, 1551 (1954); *Chem. Abstr.*, **49**, 11571 (1955). (b) R. Y. Levina, V. K. Daukshas, and T. P. Surikova, *Zh. Obshch. Khim.*, **30**, 2145 (1960); *Chem. Abstr.*, **55**, 8317 (1961).

(6) A. F. Thomas and M. Stoll, *Chem. Ind. (London)*, 1491 (1963).

pmr and refractive index studies that the hydrocarbon product of the reaction consisted of **2** and **3** in approximately equal amounts.



We have found that the decomposition of the Grignard complex is a most critical step in this reaction. When cold aqueous ammonium chloride solution or even ice-water<sup>3</sup> was added to the reaction mixture, poor variable yields of dienes were obtained.<sup>7,8</sup> The major product was a high-boiling material whose pmr spectrum showed strong signals at 0.9–1.0 and 5.1 ppm. These signals would be consistent with a substance arising from polymerization of the dienes, but this complex material has not been examined further. However, when the Grignard reaction mixture was decomposed by adding it to ice-water,<sup>9</sup> the carbinol **1** was isolated almost quantitatively.

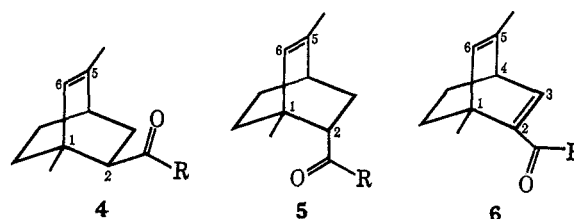
Conditions for acid-catalyzed dehydration of **1** also proved to be critical. Because we initially assumed that the heteroannular diene **3** would take no part in the Diels–Alder reaction under mild conditions,<sup>10,11</sup> we spent some time investigating the possibility of a selective dehydration of **1** to **2**. Mild conditions, such as a solution of **1** in acetic acid or a two-phase system of 5% aqueous sulfuric or perchloric acid shaken with an ethereal solution of **1**, always gave approximately 1:1 mixtures of **2** and **3**. On the other hand, stronger acids, such as a trace of sulfuric or perchloric acid in acetic acid, gave **2**, together with varying quantities of high-boiling material whose pmr spectrum strongly resembled that of the “polymer” observed on decomposition of the Grignard reaction referred to above. The yields of **3** under these conditions were notably diminished, not because of any selective formation of **2**, but because of a more rapid decomposition of **3** to “polymer.” Thus, when an approximate equimolar mixture of **1**, **2** and **3** was treated under these strong acid conditions, the product again contained **2** (in reduced amount) and “polymer” with only a trace of **3**.

Further studies on methods of selective formation of **2** (e.g., base-catalyzed E2 elimination of esters derived from **1**) were not pursued when it was found that diene **3** could be forced to participate almost quantitatively in the Diels–Alder reaction under relatively mild conditions.

**The Adducts with 1,3-Dimethyl-1,3-cyclohexadiene.**—The 1:1 diene mixture was refluxed with methyl vinyl ketone or methyl acrylate containing a trace of hydroquinone in each case. After 3 hr the pmr spectrum of the crude product indicated that all of **2** but virtually none of **3** had reacted. After 14 hr, however,

no trace of either diene remained, but a very high yield of adduct (based on the total diene mixture) was obtained—90–95% with methyl vinyl ketone and 75–85% with methyl acrylate. The slow conversion of **3** into adduct under the reaction conditions was shown to be heat dependent, rather than catalyzed by the weakly acidic hydroquinone, when a similar run with methyl vinyl ketone in the absence of hydroquinone also effected 90% conversion into adduct.<sup>12–14</sup>

This product obtained from the prolonged reaction of dienes **2** and **3** with methyl vinyl ketone appeared to be homogeneous by pmr, but vapor phase chromatography (vpc) established the presence of two compounds (**4a** and **5a**) in a ratio of about 8:1. Treatment of this



- a, R = Me  
b, R = OMe  
c, R = OH  
d, R = OEt

mixture with sodium methoxide in methanol gave the same two compounds (identical retention times by vpc) but in a ratio of 3:1, respectively. This confirmed the epimeric *endo*–*exo* relationship of the adducts and also that the major adduct was the more stable.

Similarly, dienes **2** and **3** with refluxing methyl acrylate gave a mixture of adducts **4b** and **5b** in the ratio of 8:1 approximately (pmr and vpc). Alkaline hydrolysis of this mixture gave a solid product from which the major acid **4c** was obtained by fractional crystallization. Addition of methyllithium to a solution of the crude hydrolysis product in ether gave a mixture of ketones **4a** and **5a** in an 8:1 ratio, thus interrelating the two adducts and confirming the analogous modes of reaction of the two dienophiles. An alternative approach to interrelating **4a** with **4c** by a haloform reaction of the former was less rewarding. The crude product did contain up to 60% **4c** (by pmr) but was contaminated by other unidentified acidic materials.

The *endo* configurations of the acetyl and methoxycarbonyl groups in the major adducts (**4a** and **4b**) were suggested by pmr studies initially, and confirmed later by acid-catalyzed lactonization of **4c** (see below). In the pmr spectra (Table I) of the major adducts **4**, the shielding of the R groups by the double bond and of the olefinic proton (H<sub>6</sub>) by the carbonyl group indicated<sup>15</sup> the *endo* configuration.

Treatment of **4c** with hot aqueous formic acid gave in 73% yield a product whose spectral properties were consistent with **7**. In particular, the C<sub>5</sub>-methyl group

(7) Similar problems have been encountered in Grignard reactions with some 2,3-disubstituted 2-cyclohexenones.<sup>8</sup>

(8) J. A. Marshall, N. Cohen, and A. R. Hochstetler, *J. Amer. Chem. Soc.*, **88**, 3408 (1966).

(9) von Auwers<sup>2</sup> isolated carbinol **1** by adding the reaction mixture to cold aqueous ammonium chloride solution, but the significance of this reverse addition was apparently not realized by later workers who were unable to isolate **1**.

(10) For example, 3-methylenecyclohexene gives no adduct with maleic anhydride or benzoquinone.<sup>11</sup>

(11) I. N. Nazarov and N. V. Kuznetsov, *Dokl. Akad. Nauk SSSR*, **111**, 358 (1956); *Chem. Abstr.*, **51**, 9504 (1957).

(12) Other heteroannular dienes of type **3**, e.g.,  $\beta$ -phellandrene<sup>12</sup> and abietic acid,<sup>14</sup> have also been persuaded to yield adducts with maleic anhydride, but under more forcing conditions and generally in much poorer yields than in the present case.

(13) N. F. Goodway and T. F. West, *J. Chem. Soc.*, 2028 (1938).

(14) L. Ruzicka, P. J. Ankersmit, and B. Frank, *Helv. Chim. Acta*, **15**, 1289 (1932).

(15) A. A. Othman, M. A. Qasseem, and N. A. J. Rogers, *Tetrahedron*, **23**, 87 (1967).

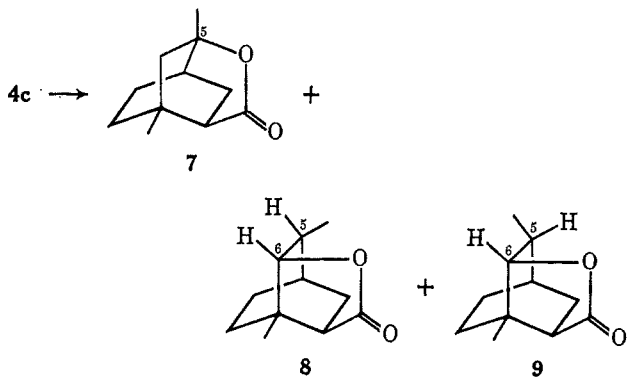
TABLE I  
PMR SPECTRA<sup>a</sup> OF ADDUCTS OF 2 AND DERIVATIVES

|                 | H <sub>5</sub> <sup>b</sup> | R                     | C <sub>1</sub> -methyl singlet | C <sub>5</sub> methyl <sup>c</sup> |
|-----------------|-----------------------------|-----------------------|--------------------------------|------------------------------------|
| 4a              | 5.51                        | 1.90 s                | 1.09                           | 1.80                               |
| 5a              | 5.51                        | 2.10 s                | 1.12                           | 1.75                               |
| 4b              | 5.45                        | 3.55 s                | 1.09                           | 1.80                               |
| 5b              | 5.56                        | 3.61 s                | 1.06                           | 1.75                               |
| 4c              | 5.48                        | 10.64 br <sup>d</sup> | 1.19                           | 1.80                               |
| 5c              | 5.57                        | 10.64 br <sup>d</sup> | 1.18                           | 1.77                               |
| 7               |                             |                       | 1.01                           | 1.37 s                             |
| 8               | 4.07 d (6.8)                |                       | 1.05                           | 1.01 d (7.3)                       |
| 6c <sup>e</sup> | 5.53                        | 12.09 br <sup>d</sup> | 1.68                           | 1.74                               |

<sup>a</sup> Determined in CCl<sub>4</sub>. Chemical shifts in parts per million downfield from TMS as internal standard with multiplicity and coupling constants (hertz) shown or discussed in footnotes. <sup>b</sup> This proton gave rise to a broad singlet,  $W_{1/2} = 4.5$  Hz except where indicated otherwise. <sup>c</sup> A doublet with  $J = 2$  Hz except where indicated otherwise. <sup>d</sup> Removed after shaking with D<sub>2</sub>O. <sup>e</sup> The other olefinic proton (H<sub>3</sub>) occurred at 7.33 as a doublet ( $J = 6.5$  Hz) while H<sub>4</sub> appeared as a multiplet at 3.34, clearly separated from other signals.

gave rise to a singlet at 1.37 ppm in the pmr spectrum and no signals occurred downfield from 2.5 ppm. Furthermore, the ir maximum in carbon tetrachloride at 1765 cm<sup>-1</sup> indicated a  $\delta$ -lactone, in excellent agreement with studies of Wilder and Winston,<sup>16</sup> who report  $5.67 \pm 0.03 \mu$  ( $1765 \pm 10$  cm<sup>-1</sup>) for a wide variety of  $\delta$ -lactones;  $\gamma$ -lactones are predicted to absorb near 5.60  $\mu$  ( $1785$  cm<sup>-1</sup>) in the same solvent.<sup>17</sup>

Lactonization of **4c** with hot anhydrous formic acid containing concentrated sulfuric acid, in a manner



analogous to that employed with diacid **10**,<sup>18</sup> gave a mixture consisting of four compounds (A, B, C, and D) in the ratio of 0.2:1:3:1 approximately (vpc). A was present in only minor amount and was not identified, while B corresponded to  $\delta$ -lactone **7**. The major constituent C showed an ir maximum at 1781 cm<sup>-1</sup> indicating a  $\gamma$ -lactone. Its pmr spectrum contained a doublet at 4.07 ppm whose coupling constant of 6.8 Hz was consistent with the configuration at C<sub>5</sub> represented in **8**, the product expected<sup>19</sup> from a "rearside" or *trans* protonation<sup>20</sup> illustrated in Scheme I. Double irradiation

(16) P. Wilder and A. Winston, *J. Amer. Chem. Soc.*, **77**, 5598 (1955).

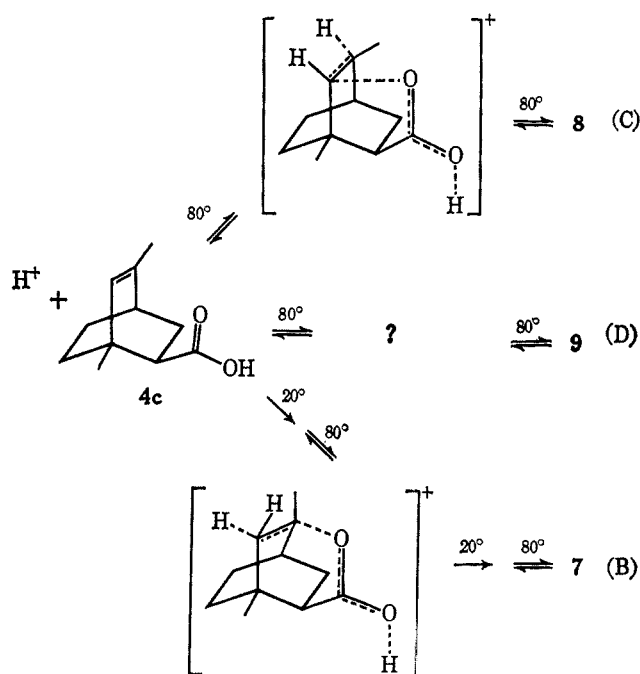
(17) W. R. Boehme, E. Schipper, W. G. Scharpf, and J. Nichols, *ibid.*, **80**, 5488 (1958).

(18) N. J. Halbrook, R. V. Lawrence, R. L. Dressler, R. C. Blackstone, and W. Herz, *J. Org. Chem.*, **29**, 1017 (1964).

(19) M. F. Ansell and M. H. Palmer, *Quart. Rev. (London)*, **18**, 211 (1964).

(20) Similarly, the appearance of a doublet at  $\tau$  4.59 ( $J = 6$  Hz) in the pmr spectrum of lactone **11** led to the assignment<sup>18</sup> of the configuration at C<sub>1</sub>, as shown.

SCHEME I



tion experiments confirmed that H<sub>5</sub> was responsible both for the doublet at 4.07 ppm, assigned to H<sub>6</sub>, and for the methyl doublet, when irradiation at 1.95 ppm collapsed each to a singlet in separate experiments. The fourth component D which could not be separated from C appeared to be also a  $\gamma$ -lactone (ir) probably isomeric with the latter. The main difference in the pmr spectrum was the presence of a broad singlet at 3.63 ppm which could be assigned to H<sub>6</sub> in  $\gamma$ -lactone **9** where the dihedral angle between H<sub>6</sub> and H<sub>5</sub> is almost 90°. This assignment of structure **9** to D must nevertheless be regarded as speculative until a purer sample is available.

A similar mechanism (Scheme I) possibly operates in the formation of **7**, which was shown to be a product of kinetic control by two further experiments. First, treatment of **4c** with cold anhydrous formic acid containing concentrated sulfuric acid gave  $\delta$ -lactone **7** in 80% yield. Second, treatment of **7** with hot anhydrous formic acid as described for **4c** gave a mixture of the same four compounds (A, B, C, and D) in similar proportion (by vpc).

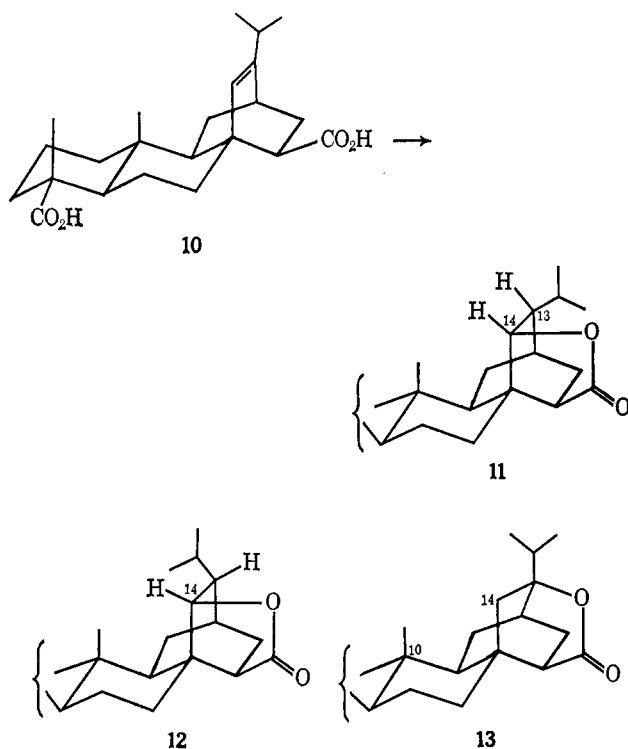
The mechanism shown in Scheme I for the formation of **8** from **7** via acid **4c** is preferred to the alternative direct conversion of **7** into **8** incorporating a 1,2-hydride shift.

It would be unwise to regard the formation of **8** under such strongly acidic conditions as evidence for the *endo* configuration in the major Diels-Alder adduct, in view of the fact that such conditions could promote epimerization of the *exo* isomer **5c** to **4c** before lactonization, or could possibly convert **5c** into lactonic products by rearrangement.<sup>15</sup> However, the lactone **7** represents more reasonable confirmation of the *endo* configuration in the major adducts (**4**) because of its formation under much milder conditions, which would not be expected to promote skeletal rearrangements. Lactone **7** appears to be the first example of the isolation of such  $\delta$ -lactones in the bicyclo[2.2.2]octane series. The structure of an

iodo- $\delta$ -lactone reported earlier<sup>17</sup> rests on an ir spectrum alone and its isolation could not be repeated.<sup>21</sup>

Our isolation of **7** in good yield prompted us to reexamine the lactonization of the diterpene derivative **10** under milder conditions than were previously used,<sup>18</sup> with a view to obtaining or detecting the corresponding  $\delta$ -lactone **13**. The requirement of structure **13** that the isopropyl group occupy the hindered side of the molecule appears from models to be of little consequence, because the twisting of the bicyclooctane ring system to form a  $\delta$ -lactone virtually eliminates any steric crowding of the isopropyl group. Furthermore, this same twisting does not appear from models to affect, or to be affected by, the rigid A and B rings. We were thus reasonably satisfied that **13** would not be in itself too unstable a molecule but did feel that hindrance to protonation at C<sub>14</sub> by the methyl group at C<sub>10</sub> could well be significant enough to prevent formation of **13** under the equilibration conditions of lactonization.

With some reservation then, we treated the diacid **10**<sup>22</sup> with acid under various conditions. Cold formic



acid for 9 hr had no effect while cold formic in the presence of perchloric acid or hot aqueous formic acids gave products whose ir spectra showed the presence of varying amounts of  $\gamma$ -lactone (1780  $\text{cm}^{-1}$ ) but no absorption due to  $\delta$ -lactone. One interesting feature emerged from the pmr spectra of the crude lactones. As well as the doublet at 4.59 (H<sub>14</sub> in **11**), a broad singlet (approximately one-third the intensity of the doublet) appeared at 4.37 ppm and could possibly be assigned to H<sub>14</sub> in the epimer **12** by analogy with **9** above.

Although the point of attachment (C<sub>2</sub>) of the carbonyl-containing group in the adducts **4** and **5** is inferred from the structures of the lactones **7** and **8**, it was verified by examination of the reaction of **2** with propiolic acid and ethyl propiolate, which should react

as dienophiles in the same sense as ethyl acrylate.<sup>23</sup> The only product isolated in low yield from the reaction with propiolic acid was 2,4-dimethylbenzoic acid, formed by an Alder-Rickert reaction<sup>24</sup> on the intermediate adduct **6c**. The latter was not isolated in this case, but could be detected in the crude product whose pmr spectrum showed a second olefinic proton as a doublet ( $J = 6.5$  Hz) downfield at 7.33 ppm which was assigned to H<sub>3</sub>. The low yield in this reaction was attributed mainly to the significant decomposition of the dienes **2** and **3** under the acidic reaction conditions.

On the other hand, the reaction of the diene mixture with ethyl propiolate proved far more satisfactory. The product consisted of a mixture of adduct **6d** and ethyl 2,4-dimethylbenzoate (4:1) together with unreacted dienes. However, alkaline hydrolysis of this mixture under reflux promoted further Alder-Rickert reaction to give an acidic product consisting of **6c** and 2,4-dimethylbenzoic acid (2:1).

A noteworthy feature of the pmr spectrum of **6c** was the appearance of the C<sub>1</sub> methyl at 1.68 ppm, strongly deshielded by the coplanar carboxylic acid group. This clear demonstration of the vicinal relationship of the two groups, together with the formation of 2,4-dimethylbenzoic acid, firmly established the structure of **6c**. Final proof of structure of the vinyl ketone and acrylate adducts was provided by the reduction of **6c** with lithium-ammonia to a 1:1 mixture of acids, identified as **4c** and **5c** by pmr and by conversion into lactone **7** in excellent yield (based on **4c**).

### Experimental Section<sup>25</sup>

**1,3-Dimethyl-2-cyclohexen-1-ol (1).**—A solution of 110 g of 3-methyl-2-cyclohexen-1-one,<sup>26</sup> bp 82–85° (12 mm), in 110 ml of ether was added dropwise during 1 hr to a stirred solution of methylmagnesium iodide (1.3 equiv) in 1000 ml of ether at 0°. The mixture was refluxed for 4 hr, then poured slowly with stirring into 2.5 l. of water and ice. The organic phase was combined with two 300-ml portions of ether extractions of the aqueous phase, then dried and evaporated to give alcohol **1**: bp 68° (5 mm) [lit.<sup>2</sup> bp 75° (15 mm)]; pmr  $\delta$  5.32 (broad s, 1, H<sub>2</sub>), 2.95 (s, 1, OH), 1.64 (broad s, 3, vinyl methyl), 1.18 (s, 3, C<sub>1</sub> methyl).

**Acid-Catalyzed Dehydration of 1.**—A solution of 24 g of **1** in 200 ml of ether was shaken at 0° for 30 min with 200 ml of 5% aqueous perchloric acid; ice was added occasionally to maintain the temperature at 0°. The ether layer was washed thoroughly with water, dried, and evaporated to give a 1:1 mixture of dienes (**2** and **3**). Subsequent reactions on this mixture were performed without delay as slow decomposition was observed on keeping: pmr  $\delta$  5.86 (m, H<sub>2</sub> in **3**), 5.48 (q, H<sub>2</sub> in **2**), 5.27 (m, H<sub>4</sub> in **2**), 4.59 (s, C=CH<sub>2</sub> in **3**), 1.77 (m, overlapping C<sub>1</sub> methyls of **2** and **3**), 1.67 (d, C<sub>2</sub> methyl in **2**).

**Diels-Alder Reaction of Dienes 2 and 3. A. With Methyl Vinyl Ketone.**—A mixture of 15 g of dienes and 30 g of redistilled methyl vinyl ketone containing 0.3 g of hydroquinone was heated

(23) W. Herz, R. C. Blackstone, and M. G. Nair, *J. Org. Chem.*, **31**, 1800 (1966).

(24) K. Alder and H. F. Rickert, *Ann. Chem.*, **524**, 180 (1936); *Ber.*, **70**, 1354, 1364 (1937).

(25) Melting points are uncorrected. Analyses are by the Australian Microanalytical Service, Melbourne. Infrared spectra were measured on a Perkin-Elmer 337 grating infracord spectrophotometer for carbon tetrachloride solutions unless otherwise stated. Pmr spectra were recorded on a Varian A-60 spectrometer using 8–10% solutions in carbon tetrachloride unless otherwise stated. Double irradiation experiments were carried out using a Varian Model V-6058A spin decoupler. A Perkin-Elmer 880 gas chromatograph was used for vpc analysis with nitrogen carrier gas at a flow rate of 40 ml/min. Columns were 10 ft  $\times$  0.125 in. of either 5% Ucon or 5% Hyprose on Chromosorb W (80–100 mesh).

(26) M. W. Cronyn and G. H. Riesser, *J. Amer. Chem. Soc.*, **75**, 1664 (1953).

(21) H. W. Whitlock, *J. Amer. Chem. Soc.*, **84**, 3412 (1962).

(22) We are grateful to Professor Werner Herz for a generous sample of this compound.

under reflux for 14 hr. The excess methyl vinyl ketone was removed under reduced pressure to give 26 g of an oil which showed two peaks (8:1) by vpc (5% Ucon, 130°) of retention times 9.7 and 8.3 min assigned to ketones **4a** and **5a**, respectively:  $\nu$  1707  $\text{cm}^{-1}$  (ketone); pmr signals corresponding to both ketones (see Table I). A similar run in the absence of hydroquinone gave an identical crude product in 90% yield.

Distillation of the crude oil in either case gave only about 75% recovery of a colorless product, bp 75° (0.5 mm), virtually identical with the crude material by vpc and pmr. The decreased yield was accounted for by a high-boiling residue, possibly arising by polymerization of the dienes (from a reverse Diels-Alder) at the relatively high bath temperature of 140° during distillation. As a result, most experiments on **4a** (see below) were carried out on undistilled material.

The ketone **4a** formed a dinitrophenylhydrazone derivative as yellow plates: mp 132.5–133°. *Anal.* Calcd for  $\text{C}_{13}\text{H}_{22}\text{N}_4\text{O}_4$ : C, 60.32; H, 6.19; N, 15.63. Found: C, 60.72; H, 6.29; N, 15.26.

When 0.5 g of the above ketone mixture (8:1) was refluxed for 1 hr in 15 ml of 4.5 *M* sodium methoxide in methanol, the crude product obtained after usual work-up showed pmr signals again corresponding to **4a** and **5a** but with an increased intensity of the latter. Vpc analysis confirmed the presence of only **4a** and **5a** but in a new ratio of 3:1 which remained constant on similar treatment of the mixture for a further 4 hr.

**B. With Methyl Acrylate.**—A solution of 11.5 g of the diene mixture and 0.3 g of hydroquinone in 42 g of redistilled methyl acrylate was heated under reflux for 12 hr. The product (17.5 g) obtained by removal of the methyl acrylate under reduced pressure showed two peaks on vpc (5% Hyprose, 110°) with retention times of 2.6 and 2.3 min (8:1) while the pmr spectrum contained signals (Table I) in similar ratio corresponding to **4b** and **5b**,  $\nu$  1733  $\text{cm}^{-1}$  (ester).

**Preparation of Acid 4c.**—The mixture of esters **4b** and **5b** (10.5 g) was heated under reflux for 20 hr with 130 ml of 2 *N* aqueous ethanolic sodium hydroxide, then concentrated to remove most alcohols, acidified (10%  $\text{H}_2\text{SO}_4$ ) at 0°, and extracted with ether. The acids were extracted from the ethereal phase with 5% sodium carbonate solution and were isolated by acidification (10%  $\text{H}_2\text{SO}_4$ ) at 0° and ether extraction. Removal of the ether gave 7.5 g of a solid which afforded *endo* acid **4c** as colorless plates by fractional crystallization from 4:1 water-ethanol: mp 101°;  $\nu$  (Nujol) 1689  $\text{cm}^{-1}$  (acid). *Anal.* Calcd for  $\text{C}_{11}\text{H}_{16}\text{O}_2$ : C, 73.30; H, 8.95; O, 17.75. Found: C, 73.45; H, 8.72; O, 17.83.

**Reaction of Methylolithium with 4c and 5c.**—A solution of 0.4 g of **4c** and **5c** (8:1) in 5 ml of dry ether was added slowly with stirring to a solution of methylolithium (from 0.8 g of lithium) in 30 ml of ether at 0°. After 1 hr at 0° and 1 hr at room temperature, the ethereal solution was washed with water and sodium hydroxide solution, dried, and evaporated to give 0.4 g of a mixture of ketones **4a** and **5a**, (8:1), identical by pmr and vpc with the mixture obtained from the Diels-Alder reaction above.

**Haloform Reaction on 4a and 5a.**—Aqueous sodium hydroxide (3 *N*, 50 ml) and a solution of 15 g of potassium iodide and 7.5 g of iodine in 50 ml of water were each added dropwise simultaneously to a solution of 1.0 g of ketones **4a** and **5a** (8:1) in 100 ml of dioxane with stirring over a period of 1.5 hr; the stirring was continued for a further 2.5 hr. The mixture was concentrated to 50 ml under reduced pressure, diluted with 100 ml of water, and then treated with solid sodium metabisulfite followed by dilute  $\text{H}_2\text{SO}_4$  at 0°. The precipitated acids were taken up into ether and then extracted with 5% sodium carbonate solution and recovered by acidification (2 *N*  $\text{H}_2\text{SO}_4$ ) at 0° and ether extraction to give 0.65 g of product whose pmr spectrum indicated the presence of about 60% **4c**.

**Lactonization Experiments on 4c. A. With Aqueous Formic Acid.**—An 8:1 mixture of **4c** and **5c** (2.4 g) was added to 70 ml of 80% formic acid and the mixture heated on a steam bath (80°) for 1.5 hr, then cooled, and added slowly to an excess of sodium bicarbonate solution. The crude neutral product (1.5 g, 73% based on **4c**), isolated by exhaustive extraction with ether, crystallized from petroleum ether as colorless square plates of **7**: mp 76–77.5°;  $\nu$  ( $\text{CCl}_4$ ) 1765 (Nujol), 1750  $\text{cm}^{-1}$  ( $\delta$ -lactone). *Anal.* Calcd for  $\text{C}_{11}\text{H}_{16}\text{O}_2$ : C, 73.30; H, 8.95; O, 17.75. Found: C, 73.27; H, 8.94; O, 17.79.

**B. With Cold Anhydrous Formic Acid.**—Purified **4c** (0.12 g) was added to 5 ml of formic acid containing 4 drops of concentrated  $\text{H}_2\text{SO}_4$  and kept at room temperature for 70 min during

which time the mixture became homogeneous. The product was worked up as above to give 0.09 g (75%) of **7**.

**C. With Hot Anhydrous Formic Acid.**—The foregoing experiment was repeated except that the mixture was heated at 80° for 1.5 hr. Similar work-up gave 0.09 g of a brown oil whose pmr spectrum contained signals corresponding to **7**, **8**, and **9**. Vpc analysis (5% Ucon, 150°) indicated the presence of four components (A, B, C, and D) with retention times of 20.9, 22.6, 24.4, and 26.8 min in a ratio of 0.2:1:3:1, respectively (assuming equimolar response). B and C could be assigned to **7** and **8**, respectively, by direct comparison.

The crude product (0.485 g) from a larger run was chromatographed on 20 g of activity I alumina from which benzene-hexane (1:3) eluted 0.125 g of a mixture of **8** and **9** which showed only two peaks on vpc corresponding to C and D (10:1). The major component **8** crystallized from pentane at –30° as colorless flakes: mp 44–46°;  $\nu$  1781  $\text{cm}^{-1}$  ( $\gamma$ -lactone). *Anal.* Calcd for  $\text{C}_{11}\text{H}_{16}\text{O}_2$ : C, 73.30; H, 8.95; O, 17.75. Found: C, 73.33; H, 9.17; O, 17.50.

Benzene-hexane (3:2) eluted 0.27 g of a complex mixture which was not investigated further.

A mixture of 0.15 g of **7** with 5 ml of formic acid and 4 drops of concentrated  $\text{H}_2\text{SO}_4$  was heated at 80° for 1.5 hr and worked up as above to yield 0.1 g of a brown oil identical (pmr, vpc) with that obtained from **4c**.

**Lactonization Experiments on 10. A. With Cold Acid.**—A mixture of 0.1 g of **10** and 5 ml of formic acid was kept at room temperature for 9 hr, then diluted with water, and the precipitate collected and dried:  $\nu$  1695  $\text{cm}^{-1}$  (acid), no lactone absorption.

A similar run with 10 drops of perchloric acid added was monitored by  $\nu$  of aliquots worked up as described above. Absorption at 1780  $\text{cm}^{-1}$  appeared after 1 hr and increased in intensity such that after 8 hr about 10% lactic material was present:  $\nu$  1780 ( $\gamma$ -lactone), 1695  $\text{cm}^{-1}$  (acid).

**B. With Hot Aqueous Acid.**—A suspension of 0.06 g of **10** in 5 ml of 80% aqueous formic acid was heated under reflux for 8 hr. The solvent was removed under reduced pressure below 30° to give a solid consisting of about 10% lactic material with  $\nu$  maxima similar to the above: pmr ( $\text{CDCl}_3$ )  $\delta$  4.59 (d,  $J = 6$  Hz,  $\text{H}_{14}$  in **11**), 4.37 (broad s,  $\text{H}_{14}$  in **12**).

**Diels-Alder Reaction of Dienes 2 and 3 with Ethyl Propiolate.**—A 1:1 mixture of 8.5 g of the dienes **2** and **3** with 2.05 g of ethyl propiolate<sup>27,28</sup> was heated at 80° until pmr analysis indicated that the latter was consumed (about 10 hr). The acetylenic proton of propiolic ester had disappeared and the characteristic doublet of the ester adduct **6d** at  $\delta$  7.12 ( $\text{H}_3$ ) was evident, together with signals corresponding to the dienes and ethyl 2,4-dimethylbenzoate. The mixture was added to a solution of 10 g of sodium hydroxide in 100 ml of ethanol-water (1:1) and refluxed for 4 hr. The solution was acidified with dilute sulfuric acid and extracted with ether from which the acidic material was extracted with aqueous sodium carbonate and thence isolated by acidification and ether extraction as a yellow solid (2.8 g) whose pmr spectrum indicated that it consisted of a 2:1 mixture of 1,5-dimethylbicyclo[2.2.2]octa-2,5-dien-2-*oic* acid (**6c**) and 2,4-dimethylbenzoic acid. The solid (1.8 g) was chromatographed on a column of 180 g of 20% silver nitrate-silica gel. Elution with benzene-hexane (1:1) afforded 0.43 g of 2,4-dimethylbenzoic acid which crystallized from benzene-hexane: mp 124.5° (lit.<sup>29</sup> mp 126°); identical by mixture melting point,  $\nu$ , and pmr with an authentic sample prepared by a haloform reaction<sup>29</sup> on 2,4-dimethylacetophenone.

Elution with benzene gave 0.17 g of a mixture of the two acids but benzene-ether (9:1) eluted 0.97 g of **6c** which crystallized from hexane as colorless prisms: melting point indefinite (decomposition<sup>30</sup> together with sublimation occurred between 110 and 130°);  $\nu$  1685  $\text{cm}^{-1}$  (acid). *Anal.* Calcd for  $\text{C}_{11}\text{H}_{14}\text{O}_2$ : C, 74.13; H, 7.92. Found: C, 74.40; H, 7.94.

**Lithium-Ammonia Reduction of 6c.**—To a suspension of 0.10 g of **6c** in 50 ml of liquid ammonia was added 0.20 g of lithium shot and the blue solution was stirred for 2 hr. After most of

(27) Prepared from acetylene dicarboxylic acid in low yield by the procedure of Perkin and Simonsen.<sup>28</sup>

(28) W. H. Perkin and J. L. Simonsen, *J. Chem. Soc.*, 91, 816 (1907).

(29) W. H. Perkin and J. F. S. Stone, *ibid.*, 2275 (1925).

(30) The pmr spectrum of a sample heated at 130° for 5 min then diluted with  $\text{CCl}_4$  contained signals due to **6c** and 2,4-dimethylbenzoic acid in a ratio of approximately 1:1 together with a sharp singlet at  $\delta$  5.33 probably due to a trace of ethylene trapped in the melt.

the ammonia had evaporated, water was added to the residue and the alkaline solution was acidified carefully at 0° with dilute HCl. The precipitate was isolated by ether extraction and evaporation of the dried extracts yielded 0.09 g of a colorless oil consisting of **4c** and **5c** in a ratio of 1:1 estimated by integration of the olefinic signals at  $\delta$  5.48 and  $\delta$  5.57.

The foregoing mixture was treated with 5 ml of formic acid containing 4 drops of concentrated H<sub>2</sub>SO<sub>4</sub> at 20° for 1 hr.

Work-up as described previously for **7** gave 0.04 g of a neutral compound, identified as **7** by pmr and vpc.

**Registry No.**—**4a**, 19990-29-5; **4a** (2,4-dinitrophenylhydrazone), 19990-30-8; **4b**, 19990-31-9; **4c**, 19990-32-0; **5a**, 19990-33-1; **5b**, 19990-34-2; **5c**, 19990-35-3; **6c**, 19990-36-4; **7**, 19990-37-5; **8**, 19990-38-6.

## Bridged Polycyclic Compounds. LVII. The Photorearrangement of 7-Methylenedibenzobicyclo[2.2.2]octadiene. The Preparation and Properties of Dibenzotricyclo[4.2.1.0<sup>1,3</sup>]octadiene<sup>1</sup>

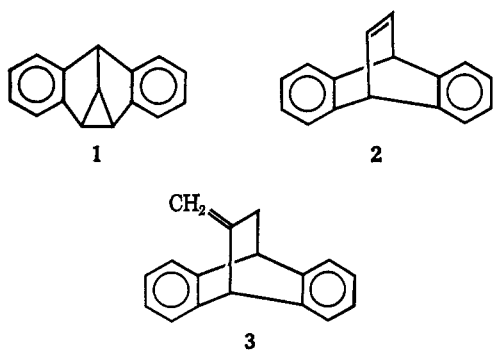
STANLEY J. CRISTOL AND GWENDOLYN O. MAYO

Department of Chemistry, University of Colorado, Boulder, Colorado 80302

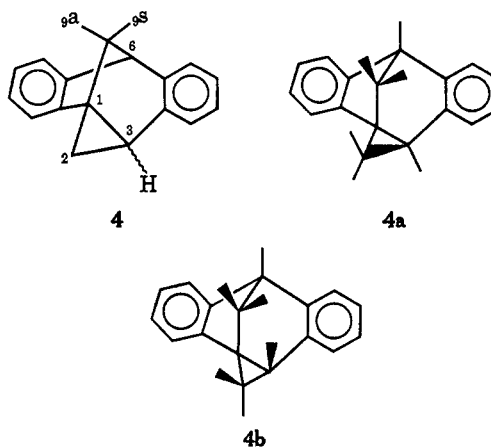
Received September 20, 1968

The photorearrangement of 7-methylenedibenzobicyclo[2.2.2]octadiene (**3**) yields dibenzotricyclo[4.2.1.0<sup>1,3</sup>]nonadiene (**4**) whose structure was determined by spectroscopic and chemical means. Upon hydrogenation cyclopropane **4** gives 5-methyldibenzobicyclo[3.2.1]octadiene (**12**). Treatment of **4** with perchloric acid in acetic acid gives dibenzobicyclo[4.2.1]nona-2,7-dien-6-ol acetate (**15**).

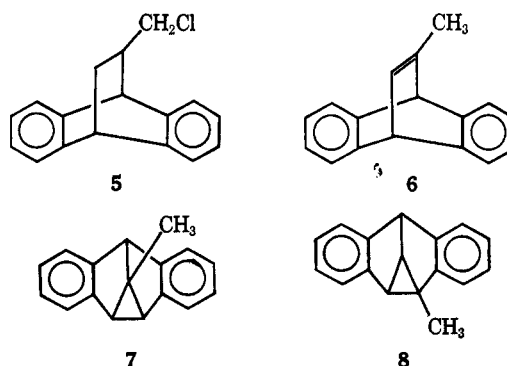
Our interest<sup>1,2</sup> in the chemistry of dibenzotricyclo[3.3.0.0<sup>2,8</sup>]octadiene (**1**) and its analogs naturally led us to the use of Ciganek's procedure<sup>3</sup> for the synthesis of **1** and its analogs by sensitized photorearrangements of dibenzobicyclo[2.2.2]octatriene (**2**) and its analogs. When 7-methylenedibenzobicyclo[2.2.2]octadiene (**3**) became available in our laboratory, we were attracted to a study of its photochemical behavior.



Irradiation of **3** in acetone gave a single compound whose pmr spectrum was initially difficult to interpret. However, at this time, a communication by Zimmerman and his coworkers appeared,<sup>4</sup> which suggested a general mechanism for the isomerization of divinylmethanes to vinylcyclopropanes. If a mechanism similar to that proposed by Zimmerman obtained in the phototransformation of **3**, one (or both) of the geometric isomers of the spirocyclopropane **4**, dibenzotricyclo[4.2.1.0<sup>1,3</sup>]nonadiene, would result. In one of the isomers (*exo* **4a**), the cyclopropane ring is *syn* to the methano bridge and, in the other (*endo* **4b**), *anti* to it. The pmr spectrum of the photoproduct is consistent with either **4a** or **4b**. The preparation of **3** by base-promoted dehydrohalo-



genation of 7-chloromethyldibenzobicyclo[2.2.2]octadiene (**5**) with potassium *t*-butoxide in dimethyl sulfoxide produced a hydrocarbon mixture that consisted largely (*ca.* 90%) of olefin **3**, contaminated with 7-methyldibenzobicyclo[2.2.2]octatriene (**6**).<sup>5</sup> When this mixture of olefins **3** and **6** was used for the photorearrangement reaction in acetone solution, two other cyclopropanes (compounds **7** and **8**)<sup>6</sup> were produced in addition to **4**.



(1) Previous paper in series: S. J. Cristol, R. J. Bopp, and A. E. Johnson, *J. Org. Chem.*, in press.

(2) See, for example, (a) S. J. Cristol and B. B. Jarvis, *J. Amer. Chem. Soc.*, **88**, 3095 (1966); **89**, 5885 (1967). (b) S. J. Cristol and B. B. Jarvis, *ibid.*, **89**, 401 (1967). (c) unpublished work of S. J. Cristol, W. Y. Lim, and A. R. Dahl.

(3) E. Ciganek, *J. Amer. Chem. Soc.*, **88**, 2882 (1966).

(4) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. S. Sherwin, *ibid.*, **89**, 3933 (1967).

(5) The powerful base utilized in the dehydrohalogenation caused prototropic equilibration of **3** and **6**.

(6) The photochemical behavior of olefin **6** and other substituted ethenanthracenes is currently under study in these laboratories. The results of these studies, as well as proofs of structure of compounds **6**, **7**, and **8**, will appear in a later paper.