

This efficient transformation of **5** to **12**, a molecule possessing four cyclopentanoid rings suitably arrayed and functionalized for possible further conversion to dodecahedrane, prompts our continuing efforts in this direction. The chemical properties of **5**, **6**, and **10** are also under active investigation.

**Acknowledgment.** This work was supported in part by grants from the National Science Foundation and Eli Lilly and Co. We wish in particular to thank Dr. David Schneider for his assistance with some of the technical aspects of this work.

(17) National Science Foundation Graduate Fellow, 1972–present.

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Received December 21, 1973

### A Multiple Cycloaddition Reaction of 9,10-Dihydrofulvalene. A New Approach to 3,4,7-Methenocyclopenta[*a*]pentalene Derivatives

Sir:

We report a multiple cycloaddition reaction of 9,10-dihydrofulvalene (**1**) which we believe has potential utility for the synthesis of polycyclic structures composed of fused five-membered rings and ultimately dodecahedrane.

9,10-Dihydrofulvalene was prepared in deuteriochloroform solution by flash vacuum pyrolysis of nickelocene and vacuum line work-up.<sup>1</sup> This solution reacted rapidly and nearly quantitatively with dimethyl acetylenedicarboxylate at 0–5° to give two isomeric monoadducts (**2** and **3**) in about equal amounts; these were isolated by preparative glpc and structures were assigned on the basis of spectral characterization.<sup>2</sup> We found for **2**:<sup>3</sup> mp 61–62°; partial ir (KBr) 2980, 1725, 1439, and 1088 cm<sup>-1</sup>; partial mass spectrum (70 eV) *m/e* (relative intensity) 272 (14, P), 240 (27), 180 (34), 153 (100), 91 (23), 79 (31); nmr (CDCl<sub>3</sub>) δ 6.05 (t, 2, *J* = 2 Hz), 3.58 (s, 3), 3.3 (m, 2), and 2.5 (m, 1). Isomer **3** was most readily distinguished from **2** on the basis of its nmr: nmr (CDCl<sub>3</sub>) δ 5.90 (t, 2, *J* = 2 Hz), 3.75 (s, 6), 3.25 (d, 2, *J* = 3 Hz), 3.0 (m, 2), 2.4–2.8 (m, 2), 2.1 (t, 2, *J* = 2 Hz); partial ir (neat) 1725, 1650, 1440, and 1110 cm<sup>-1</sup>.

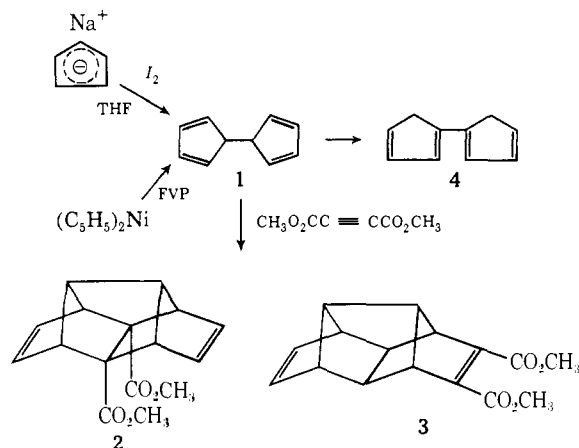
A major limitation to the above synthesis was that it was difficult and expensive to scale-up the FVP preparation of **1**. Doering and Matzner<sup>4</sup> earlier showed that sodium cyclopentadienide could be oxidatively coupled in high yield using iodine in THF at –78° to give 1,5-dihydrofulvalene (**4**) in pentane solution. Even though they reported no evidence for the 9,10-isomer **1**, it was reasonable to assume that it rearranged under the room temperature work-up conditions of their synthesis.<sup>5</sup>

(1) E. Hedaya, D. W. McNeil, P. O. Schissel, and D. J. McAdoo, *J. Amer. Chem. Soc.*, **90**, 5284 (1968).

(2) For other examples of analogous multiple cycloadditions, see (a) D. J. Cram and G. R. Knox, *J. Amer. Chem. Soc.*, **83**, 2204 (1961); (b) D. J. Cram, C. S. Montgomery, and G. R. Knox, *ibid.*, **88**, 515 (1966); (c) M. A. Battiste, L. A. Kapicak, M. Mathew, and G. J. Palenik, *Chem. Commun.*, 931 (1971).

(3) All new compounds had satisfactory elemental analyses.

(4) (a) W. v. E. Doering in "Theoretical Organic Chemistry—The Kekule Symposium," Butterworth, London, 1959, p 45; (b) E. A. Matzner, Ph.D. Thesis, Yale University, 1958.



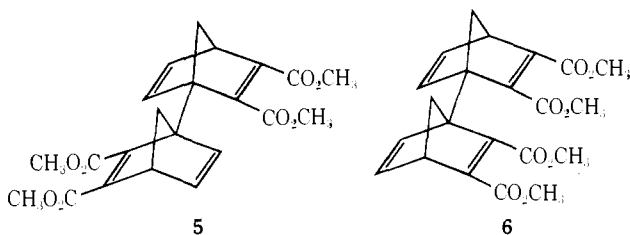
Our results described above suggested that it should be possible to trap **1** and obtain the desired monoadducts **2** and **3** by adding the dienophile after the oxidative coupling step at –78°.<sup>6</sup> This was confirmed; addition of equivalent iodine to a THF solution of sodium cyclopentadienide at –78° followed by addition of a slight excess of dimethyl acetylenedicarboxylate and slow warm-up to room temperature gave a reaction mixture from which up to 40% yields of monoadducts **2** and **3** could be isolated along with a diadduct mixture.<sup>7</sup>

The parent hydrocarbon **7** and monoolefin **8** have been obtained from **2** and **3** by relatively straightforward reactions. For example, **2** was hydrogenated over platinum oxide in methanol to give the saturated diester **9** (95% yield, mp 133–135°) which was converted to the diacid **10** (mp 277–280°; nmr (C<sub>5</sub>D<sub>5</sub>N), δ 12.4 (s, 2), 1.2–2.8 (M, 14); partial ir 3.5 br, 3.8 br, and 6.0 μ) in 63% yield by heating for 30 min in concentrated sulfuric acid on the steam bath; hydrolysis did not occur under alkaline conditions. The diester **9** could be regenerated by treating **10** with diazomethane in

(5) We showed in ref 1 that the half-life for rearrangement of 9,10-dihydrofulvalene to the 1,5-isomer was 52.3 min at 30.0° in heptane solution.

(6) E. J. Corey and coworkers have utilized a similar approach to carry out the Diels–Alder addition of 2-chloroacrylonitrile to 5-methoxymethylcyclopentadiene; E. J. Corey, N. M. Weinschenka, T. K. Schaaf, and W. Huber, *J. Amer. Chem. Soc.*, **91**, 5675 (1969).

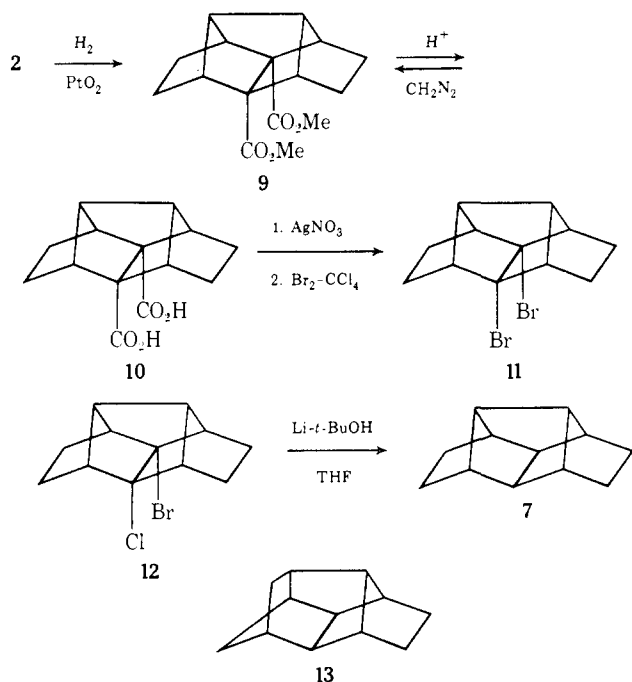
(7) The work-up involved concentration<sup>3</sup> of the THF reaction mixture to give a brown oil. Diadducts **5** and **6** were then precipitated by addi-



tion of hexane. Molecular distillation of the concentrated filtrate gave the monoadduct mixture. A second distillation using a spinning band column gave the separated isomers. Alternatively, the monoadduct isomers could be separated by selective hydrolysis in dilute sodium hydroxide. The internally substituted isomer **2** survives this treatment owing to its more hindered carboxylate groups while the externally substituted isomer **3** is converted to a soluble sodium salt. Our results can be compared with those obtained by L. Paquette and M. J. Wyratt, *J. Amer. Chem. Soc.*, **96**, 4671 (1974).

(8) The diadduct isomers were separated by crystallization from ether–pentane solutions and were not conclusively assigned. For isomer A: mp 148°; nmr (CDCl<sub>3</sub>) δ 7.00 (d, 4, *J* = 2 Hz), 3.90 (quintet, 2, *J* = 2 Hz), 3.73 (s, 12), 2.54, 2.18 (d of q, 4, *J*<sub>AB</sub> = 8 Hz, *J* = 2 Hz). For isomer B: mp 161°; nmr (CDCl<sub>3</sub>) δ 7.0 (m, 4), 4.0 (m, 2), 3.78 (s, 12), 2.35 (m, 4). The same diadducts were obtained from **1** and acetylenedicarboxylate at room temperature.

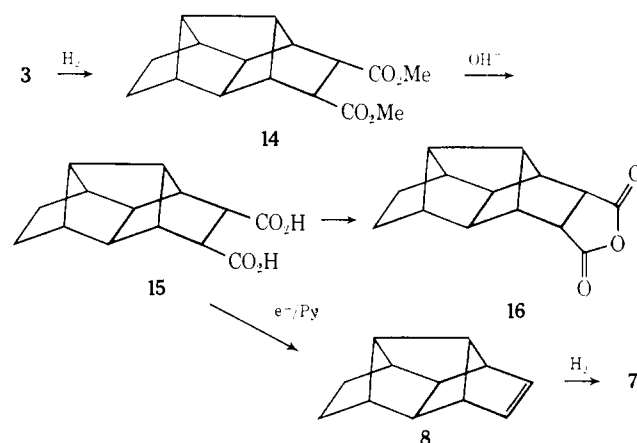
ether. The diacid **10** was subjected to a double Hunsdieker reaction by refluxing its silver salt in bromine-carbon tetrachloride solution. A 50% yield of the dibromide **11** contaminated by about 10% of bromochloro product **12** was obtained by preparative glpc: mp 170–171°; nmr (CCl<sub>4</sub>)  $\delta$  2.5 (m, 4), 2.2–1.4 (m, 10); partial ir (KBr) 3.4, 7.8, 8.3, 10.4, 12.7, 12.9, 14.0, and 14.4  $\mu$ . The dibromide reaction mixture was dehalogenated by lithium-*tert*-butyl alcohol in refluxing tetrahydrofuran to give **7**, which was isolated in 37% yield as an oil by preparative glpc: ir (neat) 3.42, 3.52, 6.85 w, 6.95 w, 7.75, 7.79, 8.35 w, 8.79 w, and 14.0 w  $\mu$ ; nmr (CDCl<sub>3</sub>)  $\delta$  2.15 (s, 6), 1.48 (s, 10). The simplicity of the nmr was striking; the spectrum taken at 220 MHz was essentially the same. In contrast, the twisted decahydromethenocyclopenta[*a*]pentalene isomer **13** has a very complex



nmr in the region  $\delta$  0.8–2.5;<sup>9,10</sup> the ir of **13** was very similar to that of **7**.<sup>10</sup>

Isomer **3** was utilized for the synthesis of monoolefin **8**. Hydrogenation over platinum oxide gave a saturated diester **14** which was hydrolyzed in 10% potassium hydroxide to give diacid **15** (~70% yield overall). The diacid was converted by trifluoroacetic anhydride to the anhydride **16** for characterization: mp 171–173°; nmr (CDCl<sub>3</sub>)  $\delta$  3.35 (m, 2), 2.7 (m, 3), 2.25 (br, s, 3), 1.8 (br, s, 2), 1.55 (s, 4); partial ir (KBr) 3.39, 3.48, 5.38, and 5.6  $\mu$ . Electrolytic decarboxylation<sup>11</sup> of the diacid **15** in 10% aqueous pyridine and a small amount of triethylamine using platinum gauze electrodes gave crude olefin **8** in about 50% yield, which was purified by preparative glpc or by column chromatography on alumina: nmr (CDCl<sub>3</sub>)  $\delta$  5.8 (t, 2, *J* = 2 Hz), 2.78 (m, 2), 2.45 (m, 3), 1.7 (m, 1), 1.4–1.6 (m,

6); partial ir (neat) 3.28, 3.40, 3.50, 6.30, 7.82, 13.83, 14.15, and 15.10  $\mu$ . Hydrogenation of **8** over platinum oxide gave the same saturated hydrocarbon **7** obtained above.



A particularly challenging synthetic application of the reactions and products described here is as starting points for a dodecahedrane synthesis. For example, **2** possesses functionality which can be potentially exploited to strategically add the additional six carbon atoms required for construction of a C<sub>20</sub> framework which subsequently can be converted to dodecahedrane by rational synthetic steps. We have found in preliminary experiments with this objective in mind that the central carbon-carbon bond of **2** can be reductively cleaved<sup>12</sup> using sodium in toluene containing trimethylsilyl chloride whereas zinc in acetic acid failed. Evidence was obtained for three isomers (endo-exo, endo-endo, and exo-exo); the exo-endo isomer could be assigned by nmr, while a tentative assignment was made for the other isomers. We anticipate that kinetically controlled, base-catalyzed isomerization of exo-carboxyl to endo-carboxyl should occur owing to steric hindrance of the endo-hydrogen, and our first results were encouraging. Various five-membered ring annulations of the double bonds also have been considered.

(12) (a) J. J. Bloomfield, R. A. Martin, and J. M. Nelke, *J. Chem. Soc., Chem. Commun.*, 97 (1972); (b) P. G. Gassman and X. Creary, *ibid.*, 1214 (1972).

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Received December 28, 1973

### Preparation of Hydridometalloboranes and Their Use as Homogeneous Catalysts

Sir:

In recent years the discovery and utility of homogeneous hydrogenation,<sup>1</sup> isomerization,<sup>2</sup> hydrosilylation,<sup>3</sup> and hydrogen-deuterium exchange<sup>4</sup> catalysts

(1) *E.g.*, see (a) J. Kwiatek in "Transition Metals in Homogeneous Catalysis," G. N. Schrauzer, Ed., Marcel Dekker, New York, N. Y., 1971, pp 13–51. (b) B. R. James, "Homogeneous Hydrogenation," Wiley, New York, N. Y., 1973.

(2) *E.g.*, see (a) R. Cramer, *J. Amer. Chem. Soc.*, **88**, 2272 (1966), and references therein; (b) R. Cramer, *Ann. N. Y. Acad. Sci.*, **172**, 507 (1971); (c) B. Hudson, P. C. Taylor, D. E. Webster, and P. B. Well, *J. Chem. Soc. A*, 37 (1968).

(3) *E.g.*, see A. J. Chalk, *Ann. N. Y. Acad. Sci.*, **172**, 533 (1971).

(9) (a) S. Winstein and R. L. Hansen, *Tetrahedron Lett.*, 1 (1960); (b) H. D. Scharf, *Tetrahedron*, **23**, 3057 (1967).

(10) We thank Professor P. v. R. Schleyer for providing us with an nmr spectrum of **10** and Dr. J. Dirlam (University of California at Los Angeles) for providing us with its corresponding ir data from the files of S. Winstein.

(11) (a) P. Radlick, R. Klein, S. Spinlock, J. J. Sims, E. E. von Tamehlen, and T. Whitesides, *Tetrahedron Lett.*, 5117 (1968); (b) H. H. Westberg and H. J. Dauben, Jr., *ibid.*, 5123 (1968).