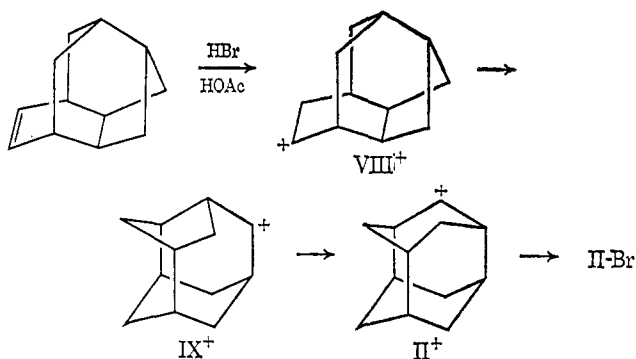


and "Allinger" (A).<sup>24b</sup> Ethanoadamantane (I) is by far the most stable C<sub>12</sub>H<sub>18</sub> isomer, being *ca.* 21–22 kcal/mol more stable than III and 6–7 kcal/mol more stable than iceane (II). This latter large difference, enhanced by the less favorable entropy of II, explains why no iceane is observed on AlBr<sub>3</sub> rearrangement. In fact, II rearranges to I under these conditions.<sup>4</sup>

Two principal routes, both involving only two 1,2-alkyl shifts, provide facile rearrangement pathways for conversion of III into I (Figure 1). The same is true for the isomerization of II into I. The carbocations involved, also favorable in energy, can be generated reversibly by hydride abstraction under the AlBr<sub>3</sub> conditions used. The dihedral angles involving the migrating bonds and the adjacent vacant carbocation orbitals are also favorable.<sup>25b</sup>

However, as Figure 1 implies, iceane (II) is a local minimum on the C<sub>12</sub>H<sub>18</sub> energy surface. The realization of this fact provided incentive for the development of the Cupas–Hodakowski synthesis of II.<sup>4</sup> Their conditions only permit sequential cationic 1,2-shifts; intermediate cation IX<sup>+</sup> can rearrange to the iceane but not



to the ethanoadamantane skeleton. Judging from the energies of the parent hydrocarbons, VIII, IX, and II, strain should be relieved in each step, VIII<sup>+</sup> → IX<sup>+</sup> and IX<sup>+</sup> → II<sup>+</sup>.

Examination of the C<sub>12</sub>H<sub>18</sub> graph also rationalizes the behavior of VI and VII on treatment with AlBr<sub>3</sub>. No pathway is available for the conversion of VI to I which does not involve a prohibitively high energy intermediate. On the other hand, much of the strain energy (~45 kcal/mol) of pentacyclic VII can be relieved by bond rupture and disproportionation; X and XI are likely products, but VI is less favorable (Table I). X

Table I

	XI	VII	X	XII
$\Delta H_f^\circ$ (calcd), kcal/mol	-16.49 (E)	+6.69 (E)	-13.73 (E)	-17.17 (E)
	-11.84 (A)	+7.42 (A)	-11.76 (A)	-17.31 (A)
Strain, kcal/mol	27.25 (E)	44.49 (E)	30.01 (E)	26.57 (E)
	32.23 (A)	45.42 (A)	32.33 (A)	26.76 (A)

is most easily convertible to I by two energetically favorable steps, X → XII and XII → I.

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### Domino Diels–Alder Reactions. I. Applications to the Rapid Construction of Polyfused Cyclopentanoid Systems

Sir:

Among several reasons for interest in a synthetic process which can achieve the multiple fusion of cyclopentane rings conveniently and in good yield is the speculation that such a method might serve as the ultimate tool for the efficient preparation of dodecahedrane. Although there are scattered reports of various ingenious techniques for the construction of representative polycyclopentanoid structures, the methodology is frequently intricate, and the overall yields are usually low.<sup>1–7</sup> One might hope to achieve appropriate carbon–carbon bond formation rapidly and to enjoy the latitude of functional group incorporation, thereby providing an opportunity for further structural elaboration if desired. The present work describes a solution to this problem for the tetracyclic case based upon a multiple cycloaddition pathway, herein designated as the domino Diels–Alder reaction.

Conceptually, the generalized domino Diels–Alder reaction involves initial *intermolecular* ( $\pi_4 + \pi_2$ ) cycloaddition of a dienophile to a 1,3-diene moiety, subsequent involvement of the newly formed olefinic center (or the residual double bond in the dienophile if originally acetylenic) in *intramolecular* ( $\pi_4 + \pi_2$ ) bonding, and continuation of this sequence if structurally permissible. The key steps, illustrated for a reaction of order [2], are exemplified by the conversion of 1 to 3.<sup>8</sup>

(1) R. B. Woodward, T. Fukunaga, and R. C. Kelly, *J. Amer. Chem. Soc.*, **86**, 3162 (1964).

(2) I. T. Jacobson, *Acta Chem. Scand.*, **21**, 2235 (1967); L. A. Paquette, G. V. Meehan, and S. J. Marshall, *J. Amer. Chem. Soc.*, **91**, 6779 (1969).

(3) R. Russo, Y. Lambert, and P. Deslongchamps, *Can. J. Chem.*, **49**, 531 (1971); C. Mercier, P. Soucy, W. Rosen, and P. Deslongchamps, *Syn. Commun.*, **3**, 161 (1973).

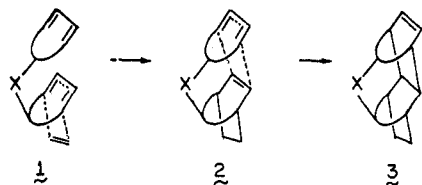
(4) R. Srinivasan, *J. Amer. Chem. Soc.*, **92**, 7542 (1970); **94**, 8117 (1972).

(5) A. de Meijere, D. Kaufmann, and O. Schallner, *Angew. Chem., Int. Ed. Engl.*, **10**, 417 (1971); *Tetrahedron Lett.*, 553 (1973).

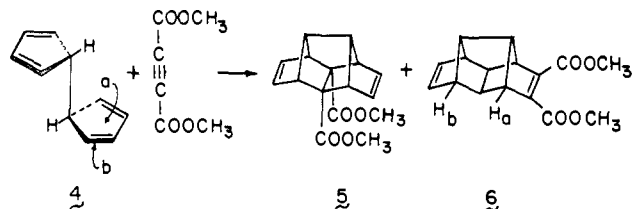
(6) P. E. Eaton and R. H. Mueller, *J. Amer. Chem. Soc.*, **94**, 1014 (1972).

(7) J. M. Edwards, I. H. Qureshi, U. Weiss, T. Akiyama, and J. V. Silverton, *J. Org. Chem.*, **38**, 2919 (1973).

(8) Higher order processes are, of course, conceivable. As early examples of order [2] behavior, we cite the reactions triggered by singlet



For the present purposes, cold ( $-78^\circ$ ) tetrahydrofuran solutions of 9,10-dihydrofulvalene (**4**), prepared



by slow addition of  $I_2$  to sodium cyclopentadienide,<sup>9a</sup> were treated with dimethyl acetylenedicarboxylate<sup>10</sup> and allowed to warm slowly to room temperature according to the procedure of Hedaya, *et al.*<sup>10</sup> Flash distillation of the ether soluble portion of the dark viscous product mixture at  $185$ – $200^\circ$  and  $0.3$  mm led to the isolation of diesters **5** ( $58\%$ ) and **6** ( $42\%$ ) in  $40\%$  combined yield. Separation of these isomers could be effected by fractional distillation through a Teflon-coated spinning band column or more conveniently by selective saponification of **6**. To effect face-to-face capture of the two cyclopentadiene moieties as in **5** requires that the acetylene initially affix itself to **4** from direction *a*; analogously, the production of **6** must involve attack along the *b* coordinate.

The pmr spectrum of **5**, mp  $61$ – $62^\circ$ ,<sup>11</sup> shows an  $-OCH_3$  singlet ( $6$  H,  $\delta$  3.56) and three other absorptions at  $6.02$  (t,  $J = 2$  Hz,  $4$  H),  $3.28$  (m,  $4$  H), and  $2.48$  (m,  $2$  H) as expected of its  $C_{2v}$  symmetry. The structure of **6** (oil,<sup>11</sup>  $C_s$  symmetry) is similarly indicated by its pmr spectrum, with multiplets of area 2 centered at  $\delta$  5.83,  $2.97$ ,  $2.58$  (v br), and  $2.13$ . The methoxyl hydrogens appear as a singlet at  $3.72$  and the  $H_a$  bridgehead protons as a doublet ( $J = 2.8$  Hz) at  $3.25$ .

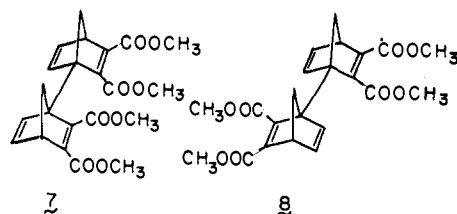
Recrystallization of the original ether insoluble material gave a highly crystalline white solid in  $3\%$  yield, the spectral properties of which warrant that it be assigned structure **7**, **8**, or a mixture of these tetraesters: pmr ( $CDCl_3$ )  $\delta$  6.90 (m,  $4$  H), 3.93 (m,  $2$  H), 3.70 (s,  $12$  H), and 2.33 (m,  $4$  H). This substance is presumably formed by twofold addition of the dienophile to 1,5-dihydrofulvalene, the fully conjugated isomer of **4** to which the latter is readily rearranged.<sup>9,12</sup>

oxygen addition to [2,2]paracyclophane [H. H. Wasserman and P. M. Keehn, *J. Amer. Chem. Soc.*, **88**, 4522 (1966)] and by exposure of 5,5'-ethylene-1,2-di-(2-furyl)ethane to dimethyl acetylenedicarboxylate [D. J. Cram and G. R. Knox, *ibid.*, **83**, 2204 (1961)]; see also H. Wynberg and R. Helder, *Tetrahedron Lett.*, 4317 (1971).

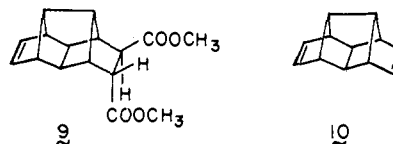
(9) (a) W. von E. Doering in "Theoretical Organic Chemistry—The Kekule Symposium," Butterworth, London, 1959, p 45; E. A. Matzner, Ph.D. Thesis, Yale University, 1958. For alternative syntheses of **4**, consult: (b) E. Hedaya, D. W. McNeil, P. Schissel, and D. J. McAdoo, *J. Amer. Chem. Soc.*, **90**, 5284 (1968); (c) K. Shen, *ibid.*, **93**, 3064 (1971).

(10) Dr. E. Hedaya informed us privately prior to the outset of our work that he had uncovered this cycloaddition reaction several years ago in connection with efforts by the Union Carbide group to characterize 9,10-dihydrofulvalene.<sup>9b</sup> As an outgrowth of an exchange of comments, recourse to simultaneous publication is being made at this time by mutual agreement; see D. McNeil, B. R. Vogt, J. J. Sudol, S. Theodoropoulos, and E. Hedaya, *J. Amer. Chem. Soc.*, **96**, 4673 (1974).

(11) Satisfactory combustion analyses have been obtained for all new compounds reported herein.

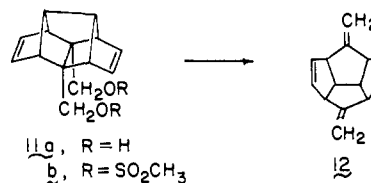


Treatment of **6** with excess  $0.581$  *N* chromous sulfate solution under nitrogen<sup>13</sup> effected selective reduction of the conjugated double bond ( $94\%$ ) with trans isomer **9**, mp  $94.0$ – $94.5^\circ$ ,<sup>11</sup> predominating by a wide margin.



Saponification of the unpurified mixture, followed by electrolytic decarboxylation (6 hr) of the diacids in  $10\%$  aqueous pyridine,<sup>14</sup> gave the crude hydrocarbon **10** in  $46.5\%$  yield. The novel structural features of this diene, seen to consist of two fused norbornene rings and to contain no less than six five-membered rings within its  $(CH)_{12}$  framework, are reflected in the symmetrical display of its pmr [ $(CDCl_3)$ :  $\delta$  5.79 (t,  $J = 2$  Hz,  $4$  H),  $2.83$  (m,  $4$  H),  $2.42$  (m,  $2$  H), and  $1.79$  (t,  $J = 2$  Hz,  $2$  H)] and cmr absorptions ( $49.12$ ,  $60.62$ ,  $61.70$ , and  $131.51$  ppm from TMS).

The central bond in **5** may be cleaved by a number of methods of which the following is illustrative. Reduction to diol **11a**, mp  $235$ – $240^\circ$  dec (rapid heating, sealed tube),<sup>11</sup> in  $95\%$  yield upon treatment of the diester with lithium aluminum hydride in ether was followed by conversion to dimesylate **11b** ( $85\%$ , mp  $130$ – $130.5^\circ$ )<sup>11</sup> through reaction with sulfene.<sup>15</sup> Subsequent heating of **11b** with sodium iodide in anhydrous hexamethylphosphoramide at  $130^\circ$  for 48 hr<sup>16</sup> afforded the desired tetraene **12**<sup>11</sup> in  $83\%$  yield. The eight olefinic protons



are seen in the pmr spectrum ( $CDCl_3$ ) as two singlets of area 4 at  $\delta$  5.28 and  $4.83$ , the remaining four hydrogens appearing as a rather narrow multiplet at  $\delta$  3.35– $3.80$ . The inherent molecular symmetry is further revealed by its cmr spectrum in  $CDCl_3$  ( $52.20$ ,  $58.78$ ,  $106.45$ ,  $135.32$ , and  $155.58$  ppm).

(12) [1,5]Sigmatropic hydrogen shifts in highly purified **4** proceed with adherence to first-order kinetics and a  $t_{1/2}$  of  $52.3$  min at  $30.0^\circ$  has been experimentally determined ( $\Delta H^\ddagger = 18.6$  kcal/mol and  $\Delta S^\ddagger = -16$  eu).<sup>9b</sup> It has been our experience that the conversion of **4** to 1,5-dihydrofulvalene is promoted by elemental iodine or by-products generated during the iodine coupling reaction (see also ref 9a).

(13) C. E. Castro, R. D. Stephens, and S. Moyé, *J. Amer. Chem. Soc.*, **88**, 4964 (1966).

(14) P. Radlick, R. Klem, S. Spurlock, J. J. Sims, E. E. van Tamelen, and T. Whitesides, *Tetrahedron Lett.*, 5117 (1968); H. H. Westberg and H. J. Dauben, Jr., *ibid.*, 5123 (1968).

(15) R. K. Crossland and K. L. Servis, *J. Org. Chem.*, **35**, 3195 (1970).

(16) For other examples of nucleophilic displacement at highly hindered carbon atoms in this medium, see L. A. Paquette, R. E. Wingard, Jr., J. C. Phillips, G. L. Thompson, L. K. Read, and J. Clardy, *J. Amer. Chem. Soc.*, **93**, 4508 (1971).

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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### 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>.

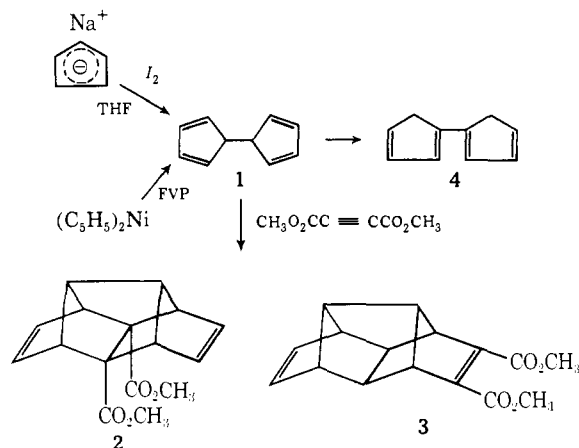
A major limitation to the above synthesis was that it was difficult and expensive to scale-up the FVP preparation of **1**. Doering and Matzner<sup>4</sup> earlier showed that sodium cyclopentadienide could be oxidatively coupled in high yield using iodine in THF at –78° to give 1,5-dihydrofulvalene (**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.



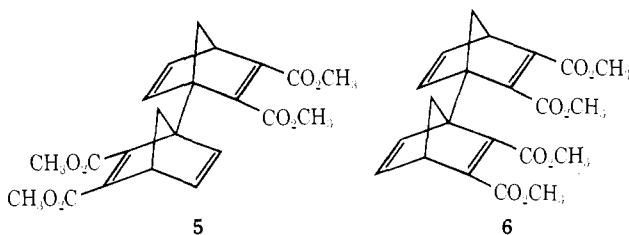
Our results described above suggested that it should be possible to trap **1** and obtain the desired monoadducts **2** and **3** by adding the dienophile after the oxidative coupling step at –78°.<sup>6</sup> This was confirmed; addition of equivalent iodine to a THF solution of sodium cyclopentadienide 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. Wyvratt, *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.