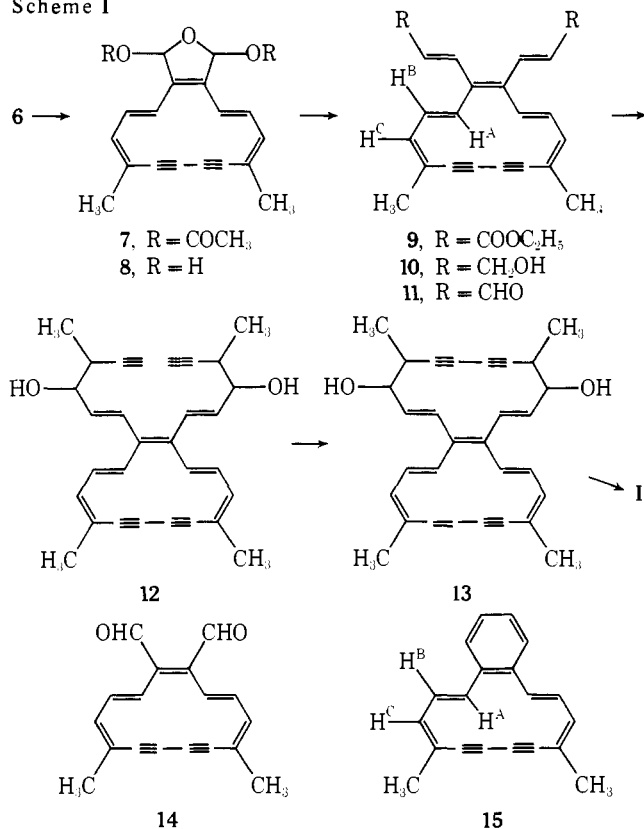


Scheme I

Table I. Some <sup>1</sup>H NMR Parameters of 9, 10, 11, 1, 15, and 6 at 100 MHz in CDCl<sub>3</sub> (τ Values; Internal Standard TMS)<sup>a</sup>

Compd	H <sup>A</sup>	H <sup>B</sup>	H <sup>C</sup>	CH <sub>3</sub>
9	8.83	2.07	2.31	7.29
10	9.24	1.88	2.22	7.28
11	8.56	← 2.06–2.34 →	7.26	7.26
1	6.18	2.13	2.69	7.52
15	5.01	2.56	2.92	7.64
6	3.48	3.69	3.28	7.94

<sup>a</sup> H<sup>A</sup> (d, *J* = 15–16 Hz), H<sup>B</sup> (dd, *J* = 7.5–10, 15–16 Hz), H<sup>C</sup> (d, *J* = 7.5–10 Hz), CH<sub>3</sub> (s), for all compounds.

(16,800), 292 (21,100), 386 (45,400), 552 sh (1050), 607 sh nm (580);  $\nu_{\max}$  (KBr) 2130 m (C≡C), 970 s (trans C=C) cm<sup>-1</sup>. Substance **1** was relatively stable, both in the solid state and in ether solution.

It has been shown previously that the <sup>1</sup>H NMR spectra of certain 1,3-bisdehydro[14]annulenes are temperature dependent, due to rotation about the trans double bonds,<sup>19</sup> and this proved to be the case with the diacetate **7**. On the other hand, the <sup>1</sup>H NMR spectra of the dehydroannulenes **9**, **10**, **11**, and **1** were essentially temperature independent in the range -60 to 100°, and showed the macrocyclic rings to exist in the indicated conformations.

Some <sup>1</sup>H NMR parameters of various 1,3-bisdehydro[14]annulenes are given in Table I. As expected, the substituted compounds **9**, **10**, and **11** are diatropic ("aromatic"), the inner H<sup>A</sup> protons resonating at unusually high field, and the outer H<sup>B</sup>, H<sup>C</sup>, and CH<sub>3</sub> protons at unusually low field. It has already been found that the diatropicity of a 1,3-bisdehydro[14]annulene is considerably reduced by fusion of a benzene ring (see **15** in Table I),<sup>20</sup> and almost completely eliminated by fusion of a [c]furan ring (see **6** in Table I).<sup>5</sup> It is evident from the NMR spectrum of **1** that fusion of a second bisdehydro[14]annulene also reduces the diamagnetic ring current of the bisdehydro[14]annulene, although to a lesser extent than benzene. The decreasing order of dia-

tropicity of the macrocyclic ring of the various compounds in Table I (**9**, **10**, **11** > **1** > **15** > **6**) is presumably a reflection of a decrease in the importance of different participating Kekulé structures of that ring.

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## References and Notes

- Unsaturated Macrocyclic Compounds. CXIV. For part CXIII, see R. T. Weavers, R. R. Jones, and F. Sondheimer, *Tetrahedron Lett.*, 1043 (1975).
- We suggest that the trivial nomenclature of dehydroannulenes containing one, two, three, four, etc. acetylenes should contain the prefix monodehydro-, bisdehydro-, trisdehydro-, tetrakisdehydro-, etc., respectively, in order to avoid confusion in the literature (see P. J. Garratt and K. Grohmann in "Houben-Weyl, Methoden der Organischen Chemie", Vol V, Part 1d, Georg Thieme Verlag, Stuttgart, 1972, pp 543–544). Unless otherwise indicated, the rings in annulenoannulenes are considered to be ortho fused.
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- Isolated by chromatography on (a) SiO<sub>2</sub> (Woelm, act II); (b) Al<sub>2</sub>O<sub>3</sub> (Woelm, act III).
- The <sup>1</sup>H NMR, electronic, and ir spectra of all new pure compounds were in accord with the assigned structures.
- The elemental composition was confirmed by the high resolution mass spectrum.
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- See R. L. Crossland and K. L. Servis, *J. Org. Chem.*, **35**, 3195 (1970).
- The conversion of **3** to **6** is based on the synthesis of related benzobisdehydroannulenes, carried out by Dr. N. Darby in these laboratories.
- Reaction of **3** with propargylaluminum bromide,<sup>11</sup> followed by coupling and then dehydration, led to the unstable bisdimethyl-**6**. We prefer to retain the methyl groups, as they confer increased stability and are useful probes for the study of ring currents by <sup>1</sup>H NMR spectrometry.
- See N. Elming and N. Clauson-Kaas, *Acta Chem. Scand.*, **6**, 535 (1952); N. Elming, *ibid.*, **6**, 578 (1952).
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- A small amount of *cis,trans*-**9** was also formed, but was readily removed by crystallization from petroleum ether-CH<sub>2</sub>Cl<sub>2</sub>.
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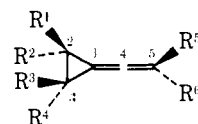
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## Cycloadditions of Alkenylenecyclopropanes with Acetylenic Dienophiles. An Exclusive Formation of the (2 + 2) Cycloadduct

Sir:

Alkenylenecyclopropane (**1**) has been shown recently by Pasto and his coworkers to react with 4-phenyl-1,2,4-triazoline-3,5-dione via a concerted [( $\pi_2 + \pi_2 + \sigma_2$ ) +  $\pi_2$ ] pathway,<sup>1</sup> while with chlorosulfonylisocyanate (CSI) **1** reacts via a dipolar intermediate followed by cyclopropane ring opening and recyclization<sup>2</sup> and with methylenemalon-dinitriles<sup>3</sup> and dichlorodifluoroethylene<sup>4</sup> in a (2 + 2) fashion via a radical mechanism. In view of the above variety of



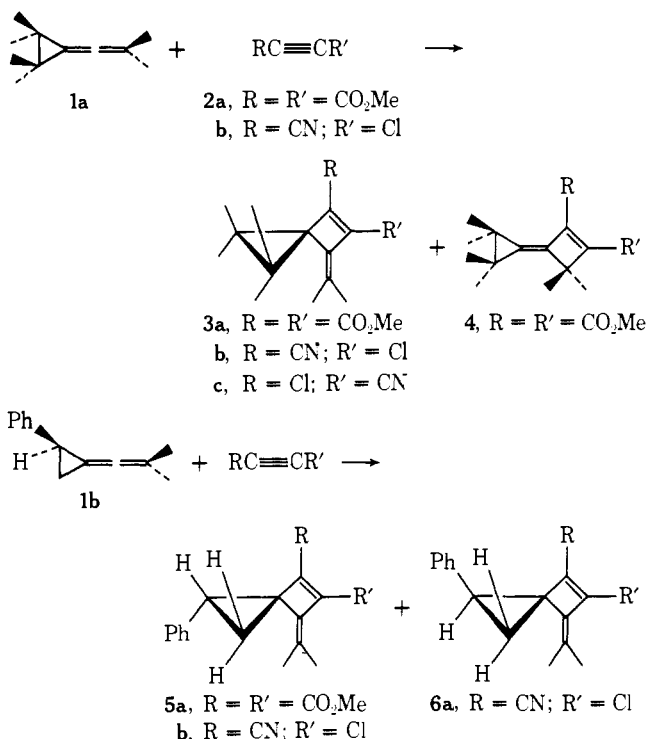
**1**

the mode of the cycloadditions of **1** we are intrigued by the behavior of **1** against acetylenic dienophiles.

The reaction of 2,2,3,3-tetramethylisobutenylidenecyclopropane (**1a**)<sup>5</sup> with dimethyl acetylenedicarboxylate (**2a**) (1:1.5 molar ratio) in benzene at 90° for 19 hr afforded two products, **3a** (mp 73–74°) and **4** (mp 46–50°) in 28 and 15% yields, respectively, after work-up on a silica gel column (benzene as eluent). Both products were 1:1 adducts on the basis of analysis and mass spectral data.<sup>6</sup> In the NMR spectrum (CCl<sub>4</sub>, 60 MHz) **3a** revealed two allylic methyl proton signals at  $\delta$  1.89 and 1.81 and four cyclopropyl methyl signals at  $\delta$  1.35 (6 H) and 1.38 (6 H) besides two ester methyl signals at  $\delta$  3.76 and 3.69, while **4** had no allylic methyl signals but saturated methyl signals at  $\delta$  1.34 (6 H) and 1.20 (12 H) as well as two ester methyl signals ( $\delta$  3.82, 6 H), and hence, **3a** and **4** were assigned as a (2 + 2) adduct at C<sub>1-4</sub> and C<sub>4-5</sub> positions of **1a**, respectively. Ir (KBr) (1750, 1720, 1670, and 1595 cm<sup>-1</sup> for **3a**; 1746, 1720, 1698, and 1612 cm<sup>-1</sup> for **4**) and uv (MeOH) absorptions ( $\lambda_{\max}$  289 (log  $\epsilon$  4.19) for **3a** and 296 nm (log  $\epsilon$  3.96) for **4**) were compatible with the assigned structures.<sup>7,8</sup>

The reaction of **1a** with chloroacetylene (**2b**) at 70° for 12 hr in benzene yielded only one (2 + 2) adduct, **3b**, mp 90.5–92° in 33% yield, which had ir (KBr) absorptions at 2220, 1675, and 1585 cm<sup>-1</sup>; uv (MeOH) absorption maximum at 278 nm (log  $\epsilon$  4.37);<sup>9</sup> and NMR (CDCl<sub>3</sub>) signals at  $\delta$  2.10, 1.87, and 1.32 in a 3:3:12 ratio, supporting the assigned structure.

On the other hand, unsymmetrically substituted 2-phenylisobutenylidenecyclopropane **1b** reacted with **2a** at 100° for 29 hr to afford one (2 + 2) adduct, **5a**, as a viscous oil (39%).<sup>10</sup> In the NMR spectrum<sup>10</sup> **5a** revealed two methyl signals at  $\delta$  1.70 and 0.67. The appearance of one of the methyl signals at a higher field such as at  $\delta$  0.67 indicated the synfacial location of the methyl group to a phenyl ring supporting the assigned structure.



The reaction of **1b** with **2b** (80°, 20 hr) gave two 1:1 adducts, **5b**, mp 103–105°, and **6**, mp 116–117° in 38 and 24% yields, whose structures were evidenced by their spectral data.<sup>11</sup>

In conclusion, the reactions of **1a,b** with **2a,b** gave exclu-

sively (2 + 2) adduct but no [( $\pi_2 + \pi_2 + \sigma_2$ ) +  $\pi_2$ ] cycloadduct. Since the examined acetylenic dienophiles have a linear molecular geometry, a simultaneous in-plane (with respect to the cyclopropanering) attack of the dienophile  $\pi$  system on C<sub>2</sub> and on the in-plane p orbital of C<sub>4</sub> may suffer from a considerable steric hindrance, and thus, [( $\pi_2 + \pi_2 + \sigma_2$ ) +  $\pi_2$ ] cycloaddition is prohibited.<sup>1</sup> However, a perpendicular attack of the acetylenes with an orthogonal orientation (against the allene moiety of **1**) on a perpendicular p orbital at C<sub>4</sub> or on an in-plane p orbital at C<sub>5</sub> should be much less sterically hindered, allowing the formation of (2 + 2) adduct.<sup>12</sup> An antifacial (to the phenyl ring) attack on **1b** by **2a** or **2b** is obviously favored and the fact that **2a** gave only **5a**, while **2b** afforded both syn- and antifacial adducts **5b** and **6** indicates a more crowded transition state geometry of the synfacial attack of **2a** than **2b**. All of the above results and the formation of two regioisomers **3a** and **4** from **1a** and **2a** indicate that the molecular geometry of attacking dienophiles is also a very important factor as well as the substituents for determining the reaction path of **1** regardless of the cycloaddition mechanism.<sup>13,14</sup>

## References and Notes

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- Compound **5a**: ir (neat) 1740, 1720, 1680, and 1590 cm<sup>-1</sup>; uv (MeOH)  $\lambda_{\max}$  217 (4.26) and 294 nm (4.07); NMR (CCl<sub>4</sub>)  $\delta$  7.25 (broad s, 5 H), 3.80 (s, 3 H), 3.73 (s, 3 H), 2.90 (m, 1 H), 1.5–1.2 (m, 2 H), 1.70 (s, 3 H), and 0.67 (s, 3 H).
- Compound **5b**: ir (KBr) 2190, 1680, and 1600 cm<sup>-1</sup>; uv (EtOH)  $\lambda_{\max}$  218 (4.05) and 280 nm (4.23); NMR (CDCl<sub>3</sub>)  $\delta$  7.20 (s, 5 H), 2.75 (t, 1 H), 1.91 (s, 3 H), 1.66 (d, 2 H), and 0.74 (s, 3 H). Compound **6**: ir (KBr) 2190, 1690, and 1600 cm<sup>-1</sup>; uv (EtOH)  $\lambda_{\max}$  218 (3.99) and 280 nm (4.18); NMR (CDCl<sub>3</sub>)  $\delta$  7.19 (s, 5 H), 2.77 (t, 1 H), 2.00 (s, 3 H), 1.70 (d, 2 H), and 1.63 (s, 3 H).
- The higher reactivity of C<sub>4</sub> and C<sub>5</sub> than C<sub>1</sub> of **1** toward electrophiles was demonstrated recently; see ref 1b and 2b.
- The sensitive nature of facial selectivity to the substituents of **1** has been postulated previously; ref 2a, b, and D. J. Pasto and J. K. Borchardt, *Tetrahedron Lett.*, 2517 (1973).
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