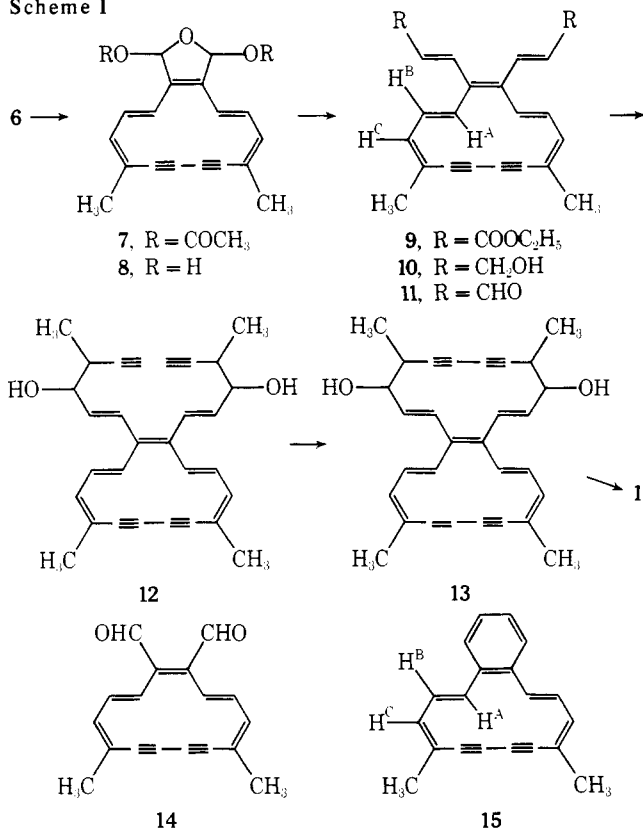


Scheme I

Table I. Some ¹H NMR Parameters of 9, 10, 11, 1, 15, and 6 at 100 MHz in CDCl₃ (τ Values; Internal Standard TMS)^a

Compd	H ^A	H ^B	H ^C	CH ₃
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

^a H^A (d, *J* = 15–16 Hz), H^B (dd, *J* = 7.5–10, 15–16 Hz), H^C (d, *J* = 7.5–10 Hz), CH₃ (s), for all compounds.

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

It has been shown previously that the ¹H NMR spectra of certain 1,3-bisdehydro[14]annulenes are temperature dependent, due to rotation about the trans double bonds,¹⁹ and this proved to be the case with the diacetate **7**. On the other hand, the ¹H 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 ¹H 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^A protons resonating at unusually high field, and the outer H^B, H^C, and CH₃ 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),²⁰ and almost completely eliminated by fusion of a [c]furan ring (see **6** in Table I).⁵ 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.

Acknowledgment. We thank the Royal Society and the Science Research Council for financial support.

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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- 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,¹¹ 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 ¹H NMR spectrometry.
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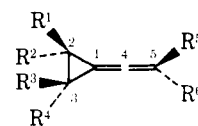
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Cycloadditions of Alkenyldenecyclopropanes with Acetylenic Dienophiles. An Exclusive Formation of the (2 + 2) Cycloadduct

Sir:

Alkenyldenecyclopropane (**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,¹ while with chlorosulfonylisocyanate (CSI) **1** reacts via a dipolar intermediate followed by cyclopropane ring opening and recyclization² and with methylenemalon-dinitriles³ and dichlorodifluoroethylene⁴ in a (2 + 2) fashion via a radical mechanism. In view of the above variety of



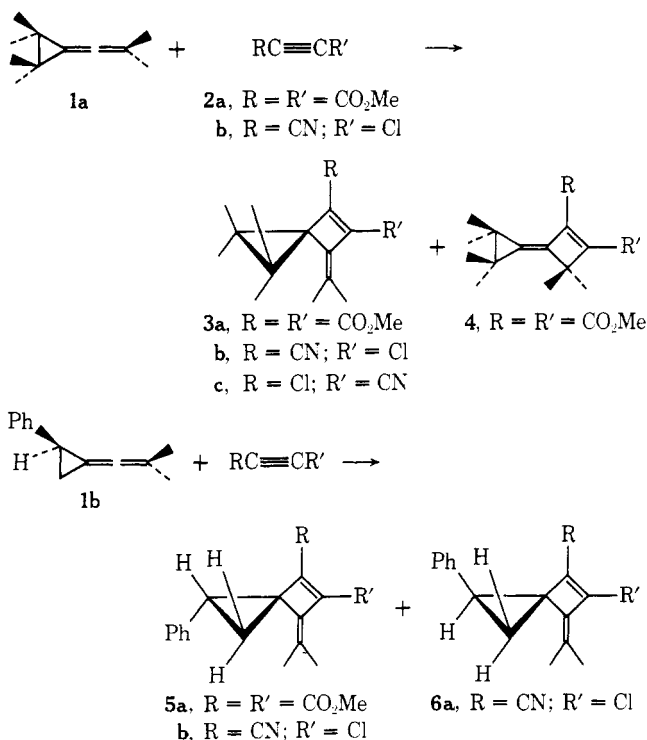
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the mode of the cycloadditions of **1** we are intrigued by the behavior of **1** against acetylenic dienophiles.

The reaction of 2,2,3,3-tetramethylisobutenylidencyclopropane (**1a**)⁵ 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.⁶ In the NMR spectrum (CCl₄, 60 MHz) **3a** revealed two allylic methyl proton signals at δ 1.89 and 1.81 and four cyclopropyl methyl signals at δ 1.35 (6 H) and 1.38 (6 H) besides two ester methyl signals at δ 3.76 and 3.69, while **4** had no allylic methyl signals but saturated methyl signals at δ 1.34 (6 H) and 1.20 (12 H) as well as two ester methyl signals (δ 3.82, 6 H), and hence, **3a** and **4** were assigned as a (2 + 2) adduct at C₁₋₄ and C₄₋₅ positions of **1a**, respectively. Ir (KBr) (1750, 1720, 1670, and 1595 cm⁻¹ for **3a**; 1746, 1720, 1698, and 1612 cm⁻¹ for **4**) and uv (MeOH) absorptions (λ_{\max} 289 (log ϵ 4.19) for **3a** and 296 nm (log ϵ 3.96) for **4**) were compatible with the assigned structures.^{7,8}

The reaction of **1a** with chlorocycloacetylene (**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⁻¹; uv (MeOH) absorption maximum at 278 nm (log ϵ 4.37);⁹ and NMR (CDCl₃) signals at δ 2.10, 1.87, and 1.32 in a 3:3:12 ratio, supporting the assigned structure.

On the other hand, unsymmetrically substituted 2-phenylisobutenylidencyclopropane **1b** reacted with **2a** at 100° for 29 hr to afford one (2 + 2) adduct, **5a**, as a viscous oil (39%).¹⁰ In the NMR spectrum¹⁰ **5a** revealed two methyl signals at δ 1.70 and 0.67. The appearance of one of the methyl signals at a higher field such as at δ 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.¹¹

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

sively (2 + 2) adduct but no [($\pi_2 + \pi_2 + \sigma_2$) + π_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 π system on C₂ and on the in-plane p orbital of C₄ may suffer from a considerable steric hindrance, and thus, [($\pi_2 + \pi_2 + \sigma_2$) + π_2] cycloaddition is prohibited.¹ However, a perpendicular attack of the acetylenes with an orthogonal orientation (against the allene moiety of **1**) on a perpendicular p orbital at C₄ or on an in-plane p orbital at C₅ should be much less sterically hindered, allowing the formation of (2 + 2) adduct.¹² 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.^{13,14}

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- (10) Compound **5a**: ir (neat) 1740, 1720, 1680, and 1590 cm⁻¹; uv (MeOH) λ_{\max} 217 (4.26) and 294 nm (4.07); NMR (CCl₄) δ 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).
- (11) Compound **5b**: ir (KBr) 2190, 1680, and 1600 cm⁻¹; uv (EtOH) λ_{\max} 218 (4.05) and 280 nm (4.23); NMR (CDCl₃) δ 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⁻¹; uv (EtOH) λ_{\max} 218 (3.99) and 280 nm (4.18); NMR (CDCl₃) δ 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).
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