

Figure 1. Nmr spectrum at -35° of the 1-methoxy-2,8,10-tridehydro[17]annulenyli anion (**8**), measured in tetrahydrofuran- d_6 at 100 MHz.

$-\text{OCH}_3$), and 202 ($M - \text{OCH}_3 - \text{CH}$, base peak); $\lambda_{\text{max}}^{\text{EtOH}}$ 254 nm (ϵ 38,000), 289 (50,000), 298 (56,000), 402 (5300), *ca.* 455 sh (2800), *ca.* 485 sh (1800), and *ca.* 525 sh (520); $\nu_{\text{max}}^{\text{CCl}_4}$ (cm^{-1}) 2210, 2180 ($\text{C}\equiv\text{C}$), and 1600 ($\text{C}=\text{C}$); nmr spectrum (CDCl_3 , 100 MHz), complex series of bands (9 H) at τ 2.84–4.50 (olefinic protons), singlet (3 H) at 6.30 (OCH_3), and doublet (2 H) at 7.08 (H_{12} ; $J_{12,13} = 4$ Hz). Structures isomeric with **9** can be eliminated, since the position (τ 7.08) of the methylene proton resonance in the nmr spectrum (*cf.* *trans*-4-octene-1,7-diyne, τ 7.08)¹⁴ and its multiplicity show that the methylene group is situated between an acetylenic and an ethylenic bond. The presence of an enol ether grouping in **9** was confirmed by the fact that the methoxyl proton resonance has been shifted downfield by τ 0.4 as compared with **7**, and by the result of catalytic hydrogenation. This reaction (5% palladium–calcium carbonate, ethyl acetate) smoothly led to 1-methoxy-1-cycloheptadecene [mass spectrum, m/e 266 (M , base peak); $\nu_{\text{max}}^{\text{CCl}_4}$ 1662 cm^{-1} (enol ether)], hydrolyzed with dilute hydrochloric acid to cycloheptadecanone. By comparison, catalytic hydrogenation of **7** under these conditions gave methoxycycloheptadecane [mass spectrum, m/e 268 (M , base peak)].

Quenching of **8** with D_2O gave monodeuterio-**9** [mass spectrum, m/e 247, 216, and 203 (base peak)]. The formation of **9** from **8** is unexceptional, a possible mechanism being indicated in structure **8a** (arrows).

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(14) Y. Gaoni, C. C. Leznoff, and F. Sondheimer, *J. Am. Chem. Soc.*, **90**, 4940 (1968).

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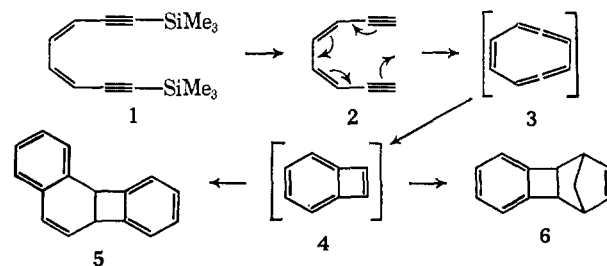
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1,2,4,5,7-Cyclooctapentaene, a Possible Intermediate in the Conversion of *cis,cis*-3,5-Octadiene-1,7-diyne to Benzocyclobutadiene Dimer¹

Sir:

We have found that *cis,cis*-3,5-octadiene-1,7-diyne (**2**) is an unstable substance and is rapidly converted into benzocyclobutadiene dimer (**5**)² in high yield. This reaction is of interest not only because it represents a synthesis of **5** from an acyclic precursor but also because it probably involves 1,2,4,5,7-cyclooctapentaene (**3**) as an intermediate.

In practice, hydrolysis of the bis(trimethylsilyl) derivative **1** ($\lambda_{\text{max}}^{\text{EtOH}}$ 292, 304, and 320 nm) in ethanol with aqueous sodium hydroxide at room temperature³ was found to result in the dienediyne **2** within a few seconds, as evidenced by the shift of the ultraviolet maxima to $\lambda_{\text{max}}^{\text{EtOH}}$ 273, 283, and 297 nm (*cf.* *cis,trans* isomer: $\lambda_{\text{max}}^{\text{EtOH}}$ 272, 282, and 296 nm; *trans,trans* isomer: $\lambda_{\text{max}}^{\text{EtOH}}$ 271, 281, and 295 nm). The ultraviolet maxima due to **2** then disappeared (half-life ~ 10 min), and were replaced by the maxima due to **5**.⁴ In a



(1) Unsaturated Eight-Membered Ring Compounds. X. For Part IX, see J. A. Elix, M. V. Sargent, and F. Sondheimer, *J. Am. Chem. Soc.*, in press.

(2) M. P. Cava and D. R. Napier, *ibid.*, **79**, 1701 (1957); **80**, 2255 (1958).

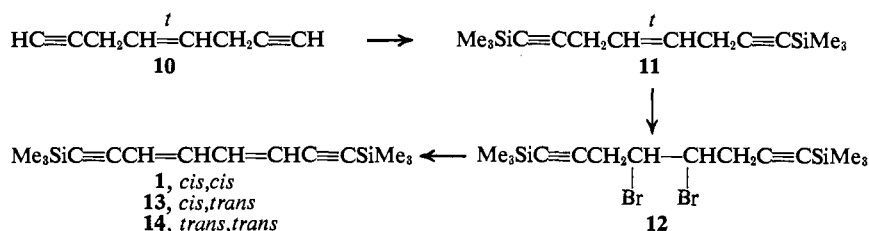
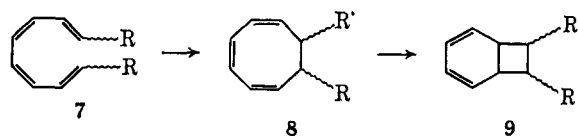
(3) See C. Eaborn and D. R. M. Walton, *J. Organometal. Chem.*, **4**, 217 (1965).

(4) The conversion of **2** into **5** is not base catalyzed, since the rate of reaction was unaffected when the mixture was acidified after **2** had been generated from **1** with base. Moreover, **5** was also obtained when the trimethylsilyl groups in **1** were removed by the silver nitrate–potassium cyanide method (H. M. Schmidt and J. F. Arens, *Rec. Trav. Chim.*, **86**, 1138 (1967)).

preparative experiment (1 hr), **5** (mp 74–75°)⁵ was isolated in 85% yield.

That the conversion of **2** to **5** proceeds by way of benzocyclobutadiene (**4**) was shown by the observation that hydrolysis of **1** in ethanol with aqueous sodium hydroxide in the presence of an excess of cyclopentadiene (40 min, room temperature) gave ~60% of the known adduct **6**⁶ (liquid; mass spectrum, molecular ion *m/e* 168). This adduct was characterized as the phenyl azide derivative (mp 131–132°; lit.⁶ mp 132–133°).

The valence isomerization of **2** to **4** presumably involves cyclization to 1,2,4,5,7-cyclooctapentaene (**3**), followed by a second cyclization to **4** [rather than a direct (2 + 2) addition of the two acetylenes in **2**]. This process is formally related to the isomerization of *cis,cis*-1,3,5,7-octatetraene and its 1,8-disubstituted de-



derivatives (**7**) to 1,3,5-cyclooctatrienes (**8**) and then to bicyclo[4.2.0]octa-2,4-dienes (**9**).⁷

An indication that the interesting diallenic cyclic hydrocarbon **3** is indeed an intermediate in the transformation of **2** to **4** was obtained from hydrogenation experiments. Platinum oxide in ethanol and aqueous sodium hydroxide was reduced by stirring in hydrogen, a solution of **1** in ethanol was added, and the hydrogenation was continued until uptake ceased. Analysis by glpc showed that one of the components of the resulting complex mixture was cyclooctane (ca. 0.5% yield), identified with an authentic sample by the mass spectrum and glpc retention time. The cyclooctane was presumably derived from the intermediate **3**, but attempts to obtain more direct evidence for this substance (e.g., by nmr and infrared spectroscopy) have not yet succeeded.

The starting material **1** was obtained as follows. Reaction of *trans*-4-octene-1,7-diyne (**10**)⁸ in tetrahydrofuran with ethylmagnesium bromide (3 molar equiv) and then with chlorotrimethylsilane (3 molar equiv) gave the bis(trimethylsilyl) derivative **11** [bp 124–128° (6 mm)]⁹ in 77% yield. Treatment of **11** with bromine (1.25 molar equiv) in chloroform at 0° led to 63% of the dibromide **12** (mp 137.5–138°),⁹ which was dehydro-

brominated with 1,5-diazabicyclo[4.3.0]non-5-ene¹⁰ (2.4 molar equiv) in ether at room temperature. Chromatography on silica gel and preparative glpc gave ~35% of the *cis,cis*-dienediene **1** [mp 35–37°; $\lambda_{\text{max}}^{\text{EtOH}}$ 292 nm (ϵ 28,700), 304 (39,500), and 320 (36,900); nmr spectrum (CDCl₃), 2 H double doublet ($J = 8$ and 2 Hz) at τ 3.09, 2 H doublet ($J = 8$ and 2 Hz) at 4.41, and 18 H singlet at 9.80],⁹ ~35% of the *cis,trans* isomer **13** [liquid; $\lambda_{\text{max}}^{\text{EtOH}}$ 291 nm (ϵ 32,100), 303 (46,000), and 319 (40,900); nmr spectrum (CDCl₃), 4 H complex multiplet at τ 2.72–4.51 and 18 H singlet at 9.80],⁹ and ~15% of the *trans,trans* isomer **14** [mp 40–42°; $\lambda_{\text{max}}^{\text{EtOH}}$ 290 nm (ϵ 37,300), 302 (58,100) and 318 (62,600); nmr spectrum (CDCl₃), 2 H double doublet ($J = 12$ and 3 Hz) at τ 3.34, 2 H double doublet ($J = 12$ and 3 Hz) at 4.28, and 18 H singlet at 9.80].⁹ Hydrolysis of **13** and **14** in ethanol with aqueous sodium hydroxide led to the corresponding unprotected dienediynes. The last-mentioned substances (together with **5**) could also be obtained directly from **10** by bromination and subsequent dehydrobromination, but the bromination step in this case proceeded in only ~10% yield.

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(10) H. Oediger, H. J. Kabbe, F. Möller, and K. Eiter, *Chem. Ber.*, **99**, 2012 (1966).

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Cyclooctatetraene and Ions Derived from It¹

Sir:

In view of the current interest in the [4*n*]annulenes, we wish to report some calculations for cyclooctatetraene (COT) and ions derived from it, using two different semiempirical SCF MO procedures that have been developed here and shown to give satisfactory results for a wide range of hydrocarbons. The first² of these is based on the Hückel σ, π approximation, the π electrons being calculated by a variant of the Pople method, while in the second, an improved version (MINDO/2^{3a}) of the MINDO^{3b} approximation, all the valence electrons are included in the SCF MO calculation. MINDO/2 differs from MINDO/1^{3b} in the choice of parameters which allows it to give good estimates of bond lengths as well as heats of formation.

(1) This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.

(2) M. J. S. Dewar and C. de Llano, *J. Am. Chem. Soc.*, **91**, 789 (1969).

(3) (a) M. J. S. Dewar and E. Haselbach, *ibid.*, in press; (b) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969).

(5) The dimer **5** was identified with an authentic sample (mp 74–75°)² by mixture melting point determination and comparison of the infrared, ultraviolet, and mass spectra.

(6) C. D. Nenitzescu, M. Avram, and D. Dinu, *Chem. Ber.*, **90**, 2541 (1957); M. P. Cava and M. J. Mitchell, *J. Am. Chem. Soc.*, **81**, 5409 (1959).

(7) See R. Huisgen, A. Dahmen, and H. Huber, *ibid.*, **89**, 7130 (1967), and references cited there.

(8) Y. Gaoni, C. C. Leznoff, and F. Sondheimer, *ibid.*, **90**, 4940 (1968).

(9) The infrared, nmr, and mass spectra were in accord with the assigned structure.