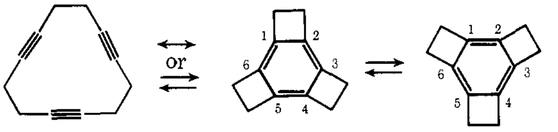
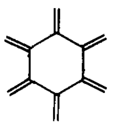
1,5,9-Cyclododecatriyne. Synthesis and Conversion to Intermediate 1,2:3,4:5,6-Tricyclobutabenzene

Sir:

Models indicate that 1,5,9-cyclododecatriyne (**1**) should exhibit significant σ-overlap of the acetylenic p orbitals in the plane of the molecule as well as π-overlap of the acetylenic p orbitals perpendicular to the molecular plane. Thus, the question arises whether **1** is capable of existence as such, whether it could be in rapid equilibrium with the highly strained 1,2:3,4:5,6-tricyclobutabenzene (**2**), or whether it might exist as an extreme canonical form of an intermediate structure with π-resonance but decreased ring strain. Compound **1** could also be viewed as a suitable precursor to the elusive **2**,[1,2] of interest for its anticipated cyclohexatrienic properties and its potential to undergo a degenerate structural isomerization **2a** $\rightleftarrows$ **2b** (detectable only by suitable labeling) via two isomeric intermediates (or transition states), the radialene **3** and its "rotamer" **4**. The latter structure has the stabilizing characteristic of an aromatic 6π system surrounded by a peripheral 6σ framework.



1 **2a** **2b**



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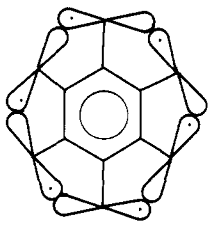

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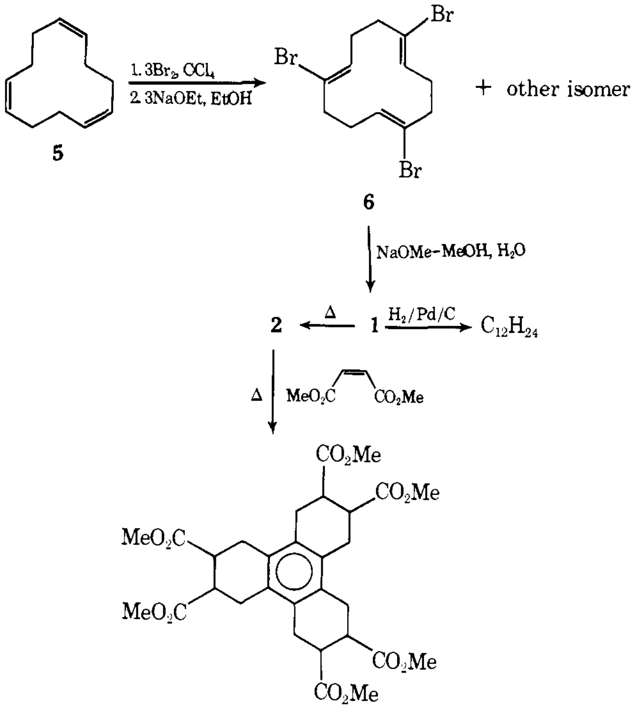
Simple HMO calculations on **1** indicate only weak (ca. 1–3 kcal) π-resonance stabilization[3] similar to the related, potentially homoaromatic *cis,cis,cis*-1,4,7-cyclononatriene[4] and *cis,cis,cis*-1,5,9-cyclododecatriene.[5] On the other hand heat of formation estimates using group equivalent techniques[6] predict the **1** to **2** interconversion to be *exothermic* by at least 23 kcal/mol. We now wish to report the synthesis and properties of this fascinating hydrocarbon, 1,5,9-cyclododecatriyne (**1**).

Our approach to **1** was modeled after the well-documented synthesis[7] of medium ring cycloalkynes from cycloalkenes by a bromination–dehydrobromination sequence. Applying this sequence to commercially available *all-trans*-cyclododecatriene led to a mixture of *sym*- and *asym*- *all-E*-trivinyl bromides.[5] These compounds proved stable to a variety of dehydrobromination conditions and *in no case* could acetylene formation be observed. Assuming that unfavorable cis-elimination was the cause of this failure to obtain **1** we turned to the all-cis-isomer **5**.[5] Bromination, followed by dehydrobromination led[8] to a 1:2 mixture of *all-Z*-trivinyl bromide **6** and the corresponding asym isomer, separated by column chromatography. The structural assignment of compound **6** (20%; colorless crystals, mp 115–116°; *m/e* 402, 400, 398, 396 (1:3:3:1); NMR (CCl_4) τ 4.70 (bt, J = 6 Hz, 3 H), 7.50 (m, 12 H)) is based on the statistical relative yield obtained, the smaller R_f value (in comparison with the less symmetrical isomer), and the relatively simple NMR spectrum.[5] Treatment of this isomer with a tenfold excess of sodium methoxide in refluxing methanol containing 2% water for 72 h led to almost quantitative conversion to 1,5,9-cyclododecatriyne (**1**)[8] isolated as colorless crystals after sublimation (50°, 0.05 mm). Interestingly, however, dehydrobromination of the unsymmetrical isomer *could not be effected* under these or even more drastic conditions. Triyne **1** (mp 89–90°) shows a sharp singlet in the NMR spectrum at τ 7.70 (CCl_4) and 7.62 (benzene-d_6), respectively, and a molecular ion base peak at *m/e* 156.0930 (calcd for $C_{12}H_{12}$: 156.0938). The electronic spectrum (λ_{max} (95% EtOH) large end absorption, 258 sh (ϵ 25.2), 264 (28.4), 267 sh (28.1), 279 (24.9) nm) is striking with vibrational structure and absorption maxima characteristic of strained benzene derivatives,[9] but extinction coefficients indicative of an acetylenic chromophore.[10,11] Proof of the triacetylene structure is provided by the ir spectrum which reveals a very weak acetylene stretching frequency at 2220 cm^{-1} and the ^{13}C NMR spectrum (δ (ppm from Me_4Si in benzene-d_6) 19.28, 80.05) with clearly acetylenic absorptions.[12] The ^{13}C–H coupling constant (ca. 131 Hz) also appears normal for propargylic moieties.[13] Catalytic hydrogenation leads to cyclododecane identical (GC, NMR, mass spectrum) with authentic material.



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Although the very strong bathochromic shifts and hundredfold increase of extinction coefficients in the electronic spectrum of **1** in comparison with acetylene[10] point to effective interaction of the three acetylene groups[14] the molecule is surprisingly stable[15] to exposure to heat (220°), light (high pressure mercury lamp), pressure (15 kbar), acid (CF_3CO_2H; addition of H_2SO_4 leads to slow decomposition), and CpCo-$(CO)_2$[16] (in refluxing *n*-octane). However, reaction of **1** with dimethyl maleate (solvent) at 230° for 16 h (sealed tube) led to the triadduct **7** as a mixture of isomers[8] (34%, semicrystalline solid; *m/e* 588.2224 (calcd for $C_{30}H_{36}O_{12}$: 588.2206); NMR (CCl_4) τ 6.34 (bs, 18 H), 6.2–8.0 (bm, 18 H); uv (Et_2O) λ_{max} large endabsorption, 267 sh, 277 sh, 290 nm; ir $\nu_{C=O}$ 1730, ν_{arom} 758 cm^{-1}). Ester hydrolysis followed by lead tetraacetate oxidation[2a] gave triphenylene, identical with authentic material.

The formation of **7** most likely proceeds via the *intermediate generation of tricyclobutabenzene* **2** followed by either stepwise ring opening to corresponding *o*-xylylenes or concerted transformation to **3** or **4**, respectively, and subsequent reaction with dimethyl maleate. It is interesting to note that the solvent recovered from this pyrolysis reaction had partially (40%) isomerized to crystalline dimethyl fumarate. In addition, controls showed that the onset of isomerization coincided with the beginning of adduct formation. Under the same conditions without any triyne present, starting material was recovered unchanged. It is tempting to associate the biradicaloids[17] **3** and/or **4** with the catalytically active species in the maleate-fumarate interconversion, although clearly other radical mechanisms are possible.[18] Clarification of this point will have to await further studies.

Current efforts are directed toward the isolation of **2**, the design of labeling experiments to identify the nature of the precursor to **7**, and the use of **1** as a template for organometallic transformations.

Acknowledgments. We thank Professors C. H. A. Seiter and K. L. Servis at the University of Southern California for the ^{13}C NMR spectra, Professor D. A. Shirley and Dr. S.-T. Lee for a PE spectrum, and the donors of the Petroleum Research Fund administered by the American Chemical Society, the Research Corporation, and the Energy Research and Development Agency for financial support.

References and Notes

(1) A dodecafluoro derivative has been claimed but no details and structural proof were provided: M. O. Riley and J. D. Park, *Tetrahedron Lett.*, 2871 (1971).

(2) For other possible approaches, see (a) R. P. Thummel, *J. Chem. Soc., Chem. Commun.*, 899 (1974); (b) E. Cuthbertson and D. D. MacNicol, *Tetrahedron Lett.*, 1893 (1975).

(3) $k = 0$, $E_\pi = 8.280\,\beta$; $k = 0.1$, $E_\pi = 8.291\,\beta$; $k = 0.2$, $E_\pi = 8.326\,\beta$; $k = 0.3$, $E_\pi = 8.388\,\beta$; $k = 0.4$, $E_\pi = 8.479$. Assuming the absence of bond angle distortions to improve overlap between the three acetylene groups in 1, the distance between the pairs of carbons in question (e.g., $C_{1,10}$, $C_{2,5}$, $C_{6,9}$) can be estimated to be 2.39 Å resulting in a k value of 0.2.

(4) K. G. Untch, *J. Am. Chem. Soc.*, **85,** 345 (1963); K. G. Untch and R. J. Kurland, *ibid.*, **85,** 346 (1963); *J. Mol. Spectrosc.*, **14,** 156 (1964); P. Radlick and S. Winstein, *J. Am. Chem. Soc.*, **85,** 344 (1963); W. R. Roth, *Justus Liebigs Ann. Chem.*, **669,** 11 (1963); W. R. Roth, W. B. Bang, P. Goebel, R. L. Sass, R. B. Turner, and A. P. Yu, *J. Am. Chem. Soc.*, **86,** 3178 (1964); S. Winstein and F. P. Lossing, *ibid.*, **86,** 4485 (1964).

(5) K. G. Untch and D. J. Martin, *J. Am. Chem. Soc.*, **87,** 3518 (1965).

(6) S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968.

(7) H. Meier, *Synthesis*, 235 (1972).

(8) All isolated new compounds gave satisfactory analytical and/or spectral data.

(9) See, for instance, M. P. Cava, A. A. Deana, and K. Muth, *J. Am. Chem. Soc.*, **82,** 2524 (1960); D. Davalian and P. J. Garratt, *ibid.*, **97,** 6883 (1975); C. J. Saward and K. P. C. Vollhardt, *Tetrahedron Lett.*, 4539 (1975).

(10) Acetylene itself shows a very weak absorption with complicated vibrational structure from 210 to 240 nm ($\epsilon \sim 0.3$): C. K. Ingold and G. W. King, *J. Chem. Soc.*, 2702, 2704, 2708, 2725, 2745 (1953). See also H. G. Viehe, "Chemistry of Acetylenes", Marcel Dekker, New York, N.Y., 1969.

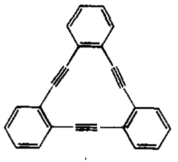
(11) Although we cannot rigorously rule out the presence of a very small amount of **2** in equilibrium with **1,** the calculations, the absence of absorptions in the ^{13}C and ^{1}H NMR spectra attributable to **2,** the similarity of the electronic spectrum with the corresponding spectra of other cyclic oligoacetylenes,[10] and the stability of **1** to reaction conditions that would be expected to lead to destruction of the four-ring argues strongly for the presence of pure **1** in solution.

(12) For comparison, the ^{13}C NMR spectrum of 2,6-octadiyne shows absorptions at 19.73, 75.80, and 77.67 ppm.

(13) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972.

(14) This is also indicated by a preliminary photoelectron spectrum which shows three close lying bands at 9.17, 9.60, and 9.84 eV. For comparison, the first bands of 1,5-hexadiyne occur at 10.48 and 10.98 eV: P. Bischof, R. Gleiter, H. Hopf, and F. T. Lenich, *J. Am. Chem. Soc.*, **97,** 5467 (1975); F. Brogli, E. Heilbronner, J. Wirz, E. Kloster-Jensen, R. G., Bergman, K. P. C. Vollhardt, and A. J. Ashe, *Helv. Chim. Acta*, **58,** 2620 (1975).

(15) The related 1,5,9-tridehydrotribenzo[12]annulene i is, not unexpectedly,



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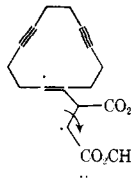

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similarly inert with respect to internal cyclization, since this process would lead to a highly strained and (in contrast to **2**) electronically destabilized (cyclobutadienoid[19]) structure: H. A. Staab and F. Graf, *Chem. Ber.*, **103,** 1107 (1970); I. D. Campbell, G. Eglinton, W. Henderson, and R. A. Raphael, *Chem. Commun.*, **87,** (1966).

(16) This compound is an efficient acetylene trimerization catalyst: W. G. L. Aalbersberg, A. J. Barkovich, R. L. Funk, R. L. Hillard III, and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, **97,** 5600 (1975); R. L. Hillard III, and K. P. C. Vollhardt, *Angew. Chem.*, **87,** 744 (1975); *Angew. Chem., Int. Ed. Engl.*, **14,** 712 (1975).

(17) J. Michl, *Top. Curr. Chem.*, **46,** 1 (1974).

(18) For instance, thermolysis of **1** could provide oligomeric radicals acting as catalysts, or, as a referee pointed out, dimethyl maleate could attack a triple bond resulting in an intermediate diradical ii. This species could then go on to cyclize to **2** and produce dimethyl fumarate in the process.

(19) K. P. C. Vollhardt, *Top. Curr. Chem.*, **59,** 113 (1975).

(20) Fellow of the Alfred P. Sloan Foundation and recipient of a Regent's Faculty Summer Fellowship.

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Topomerization of the (*Z,E*)-1,3-Diphenyl-2-cyanoallyl Anion

Sir:

Three points are of interest in connection with the topomerization of allyl anions: the geometric stability of the allyl anion, its ionic character, and the mechanism of the topomerization. The investigation of the (*Z,E*)-1,3-diphenyl-2-cyanoallyl anion (**1**) together with semiempirical and ab initio calculations provides pertinent results.

Ring opening of 2-cyano-*cis*-2,3-diphenylcyclopropyl anion (**2**) (or of the trans isomer[1,2]) afforded **1** (Scheme I), which was identified by its NMR spectrum at 5 °C. Especially the high-field absorption of the phenyl protons in para position at δ 6.5 ppm is diagnostic of the ionic character[3-6] of **1** (sodium salt in Me_2SO). The (*Z,E*) configuration[7] is revealed by the different absorptions of H^1 and H^3 at δ 5.4 and 4.65 ppm, respectively.[8]

On warming, a broadening and, at 62 ± 3 °C, the coalescence of the signals of H^1 and H^3 are observed. This is indicative of a process that exchanges the environments of these hydrogens. From a lineshape analysis[9] the following kinetic data were calculated: $k_{62^\circ C} = 100\ s^{-1}$; $\Delta G^{\ddagger}_{62^\circ C} = 16.5$ kcal/mol; $\Delta H^{\ddagger} = 12.5 \pm 4.0$ kcal/mol; $\Delta S^{\ddagger} = -12 \pm 8$ eu. Concerning the mechanism of this exchange process, the following cases have to be considered.

(1) The reaction proceeds via cyclopropyl anion **2** as an intermediate (Scheme I). This is attractive since the thermal cis–trans isomerization of butadiene is dominated by a valence isomerization via cyclobutene.[10] Likewise, according to ab initio calculations[11] the 2-methylallyl cation should prefer to topomerize via the 1-methylcyclopropyl cation rather than by rotation around the allyl cation bond.

Scheme I