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CYCLYNES
SYNTHESIS AND CHARACTERIZATION OF OCTAMETHYLCYCLODODECA-1,3,7,9-TETRAYNE.

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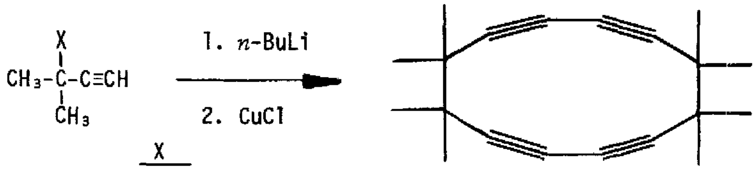
We have discovered that copper-catalyzed decomposition of the anion derived from 1a produces the stable, cyclic tetra-acetylene 2. Thus, deprotonation of tetrahydropyranyl ether 1a with 1.0 eq of *n*-BuLi in THF at -78° followed by warming overnight with a catalytic amount of CuCl gives the title compound (2) in 5% yield; chromatography on silica gel, recrystallization from ethanol, and sublimation serve to free this white, crystalline product from the large amounts of accompanying polymer. Propargylic acetate 1b also functions successfully in this reaction; however, the corresponding methyl ether (1c) and chloride (1d) did not.



$$CH_3-\overset{X}{\underset{CH_3}{C}}-C\equiv CH \xrightarrow[2.\ CuCl]{1.\ n\text{-}BuLi}$$

	X
1a	OTHP
b	OAc
c	OCH_3
d	Cl

2

Table I summarizes the physical and spectroscopic properties of tetrayne 2; the ultraviolet spectrum of 2 agrees well with that of the parent 1,3,7,9-cyclododecatetrayne reported by Sondheimer[1] (λ_{max} *ca* 236,247,263 nm). Chemical evidence for the structure of 2 includes its oxidation (RuO_4, *t*-BuOH/H_2O) to tetramethyl succinic acid[2] and its reduction (3 atm H_2, Rh/Alumina) to the completely saturated hydrocarbon 1,1,2,2,7,7,8,8-octamethylcyclododecane, some properties of which are summarized in Table II.

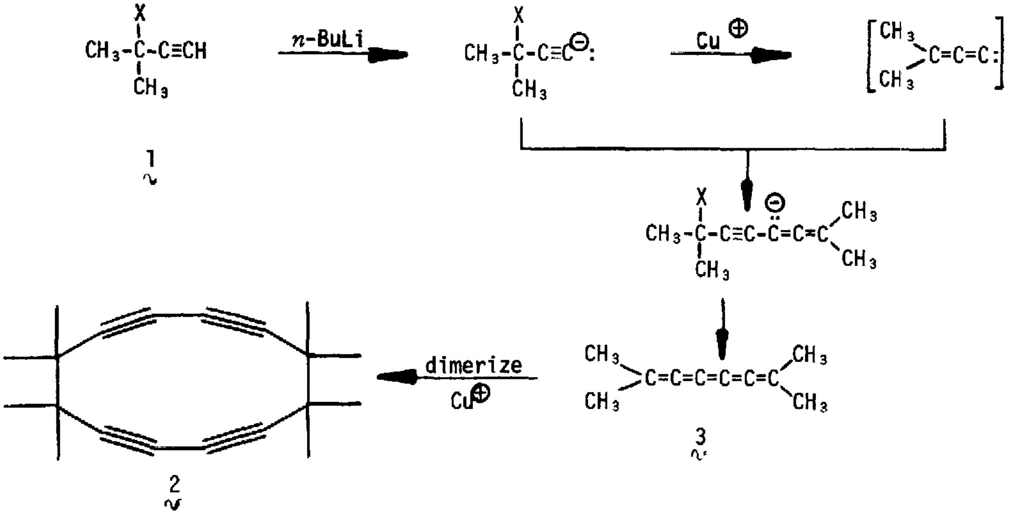
The incorporation of two 1,3-diyne units into a twelve membered ring should have interesting structural consequences. Unfortunately, the rapid polymerization of unsubstituted 1,3,7,9-cyclododecatetrayne has precluded isolation, purification, and study of the parent cyclyne. The octamethyl derivative (2), however, can be easily purified and survives unchanged even at temperatures up to 150°, both neat and in concentrated solutions. Accordingly, we have been able to examine this strained tetra-acetylene in some detail.

Preliminary X-ray crystallographic data[3] support the assignment of structure 2. All eight acetylenic carbon atoms have bond angles of *ca* 166°, and the two "bowed" diyne units lie in different planes.

The unusual electronic nature of 2 is most dramatically revealed by its He(I) photoelectron spectrum (Table I). Whereas linear diacetylenes, *eg*, $CH_3C{\equiv}C{-}C{\equiv}CCH_3$ have only two low-energy π-ionization potentials (Table III), the PES of 2 shows a substantial splitting (*ca* 0.5 ev) in both of these. Such splitting of the π-molecular orbitals could arise from bending in the diacetylene units and/or from electronic interaction between the two diynes. The U-shaped bending of a conjugated diacetylene unit will necessarily split the degeneracy of the "in-plane" and "out-of-plane" π-molecular orbitals; however, MO splittings as large as 0.5 ev have been observed[4] for strained *mono*acetylenes only in cases with a deformation from linearity at the acetylenic carbon atoms exceeding 30°. Since the bond angle at each acetylenic carbon atom in 2 deviates from linearity by only about 14°, it seems unlikely that the observed MO-splitting of *ca* 0.5 ev could result entirely from bending. Through-space and/or through bond interactions betweem the two diacetylenes could also contribute to the splitting, but 0.5 ev also seems too large for this to be the sole factor[5].

A substantial bathochromic shift in the ultraviolet spectrum of 2 (Table I) relative to that of acyclic diynes (Table III) likewise reflects the unusual electronic nature of this cyclyne[1].

The scheme below outlines a mechanism by which 2 might be formed from 1. Generation of allenylidenes and cumulenes by related γ-eliminations is well established[6]; however, the final (symmetry forbidden) cycloaddition lacks precedent to the best of our knowledge.



Two pieces of evidence support the intermediacy of 3 in this reaction. The air-sensitive, yellow pentaene[7] 3 can actually be isolated by interrupting the reaction before completion. Furthermore, purified cumulene 3 *in the presence of homogeneous Cu(I)* does indeed dimerize to tetrayne 2 in refluxing THF. Both the dimerization of 3 and the original formation of 2 from 1a fail in the absence of Cu(I).

The complete X-ray structure, MO calculations and detailed analysis of the He(I) photoelectron spectrum of 2 will be reported in due course. We are currently investigating the chemistry of both cyclyne 2 and cumulene 3.

Table I: Physical data for 5,5,6,6,11,11,12,12-octamethylcyclododeca-1,3,7,9-tetrayne (2).

mp 150° (dec., sealed capillary under N_2)	
Anal.	Calcd for $C_{20}H_{24}$: C, 90.85; H, 9.15 Found: C, 90.57; H, 9.45
mol. wt. (osmometric)	Calcd for $C_{20}H_{24}$: 264 Found: 260 ± 10
Mass spec (70 ev)	M^+ Calcd for $C_{20}H_{24}$: 264.1878 Found: 264.1880 ± 0.0003 m/e (r.a.) 264 (30), 249 (4), 234 (5), 219 (9), 181 (15), 180 (86), 165 (6), 133 (12), 132 (100), 117 (16), 91 (11)
pmr ($CDCl_3$)	δ1.18 ppm (s)
cmr (C_6D_6)	δ23.51 (CH_3), 42.59 (quaternary carbon) 70.51 and 95.44 ppm (acetylenic carbons)
ir (KBr)	2250 (C≡C), 1450, 1395, 1365 cm^{-1} (*gem*-dimethyl)
Raman (crystal)	2234 cm^{-1} (C≡C, very strong)
uv (EtOH)	λ_{max} 236 (ε720), 248 (ε770), 263 nm (ε510)
He(I) photoelectron spectrum (IP_v)[a]	8.27, 8.80, 10.72, 11.24 ev (±0.05)

[a] These are the four distinct low energy maxima, but some may correspond to more than one ionization process.[5]

Table II: Physical data for 1,1,2,2,7,7,8,8-octamethylcyclododecane

mp 54-55°	
Anal.	Calcd for $C_{20}H_{40}$: C, 85.63; H, 14.37 Found: C, 85.73; H, 14.14
pmr ($CDCl_3$)	δ0.83 (s, 24H, $-CH_3$) and 1.37 ppm (s, 16H, $-CH_2-$)
mass spec (70 ev)	M^+ at m/e 280

Table III: Spectral data for 2,4-hexadiyne ($CH_3C{\equiv}C{-}C{\equiv}CCH_3$)

uv (alc.)[a]	λ_{max} 218.5 (ε300), 226.5 (ε360), 236.0 (ε330), 250.0 nm (ε160)
He(I) photoelectron spectrum[b] (IP_v)	8.91 and 11.46 ev

[a] J. B. Armitage, C. L. Cook, N. Entwistle, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1998 (1952).

[b] F. Brogli, E. Heilbronner, F. Hornung, and E. Kloster-Jensen, *Helv. Chim. Acta*, 56, 2171 (1973).

Acknowledgements

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References and Notes

(1) R. Wolovsky and F. Sondheimer, *J. Amer. Chem. Soc.*, **87**, 5720 (1965).

(2) Tetramethylsuccinic acid was identified by comparison with an authentic sample prepared by the method of C. Fouquey and J. Jacques, *Synthesis*, 306 (1971).

(3) An X-ray crystal structure determination of tetrayne **2** has been initiated by R. Weiss and K. N. Trueblood at UCLA.

(4) H. Schmidt, A. Schweig, and A. Krebs, *Tet. Lett.*, 1471 (1974); G. Bieri, E. Heilbronner, E. Kloster-Jensen, A. Schmelzer and J. Wirz, *Helv. Chim. Acta*, **57**, 1265 (1974).

(5) Semi-empirical MO calculations based on the X-ray structure of **2** are currently underway in collaboration with Professor K. N. Houk who kindly recorded the PES of cyclyne **2**.

(6) H. D. Hartzler in "Carbenes," vol. II, R. A. Moss and M. Jones, Jr., Eds., J. Wiley and Sons, New York, N. Y., 1975, Chapter 2.

(7) The 2,7-dimethyl-2,3,4,5,6-octapentaene was identified by reduction (H_2/Rh/Alumina/-78°) to 2,7-dimethyloctane. Cumulene **3** shows a singlet in the ^{1}H-nmr spectrum ($CDCl_3$) at δ1.95 ppm and a rich uv spectrum with λ_{max}^{EtOH} 214, 226, 306, 320 [lit. λ_{max}^{EtOH} 215, 228, 308, 321: L. Skatteboel, *Tet. Lett.*, 2175 (1965)]. Rapid polymerization thwarted all attempts to isolate pentaene **3** free from solvent.