ring have been noted by Albert.[1] So far as we are aware, however, this is the first case in which a substituent has been added to the 6 position, presumably by addition to a double bond in the partially reduced ring, with subsequent further reoxidation.[2]

[1] A. Albert, "Current Trends in Heterocyclic Chemistry," A. Albert, G. M. Badger and C. W. Shoppee, eds., Academic Press, Inc., New York, N. Y., 1958, p. 20.

[2] This work was supported by the Rockefeller Foundation, the Robert A. Welch Foundation, Houston, Texas, and the National Science Foundation.

ZOÖLOGY DEPARTMENT
UNIVERSITY OF TEXAS
AUSTIN, TEXAS
C. VAN BAALEN
H. S. FORREST

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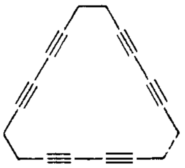
UNSATURATED MACROCYCLIC COMPOUNDS. VI. THE SYNTHESIS OF CYCLOÖCTADECA-1,3,7,9,13,15-HEXANE-5,11,17-TRIYNE, A COMPLETELY CONJUGATED EIGHTEEN-MEMBERED RING CYCLIC SYSTEM[1]

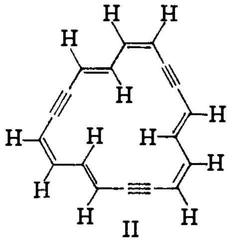
Sir:

It has been shown that the oxidative coupling of terminal diacetylenes may lead to large-ring polyacetylenes.[2,3] We have also found that certain linear 1,5-enynes ($-C\equiv C-CH_2CH_2-CH=CH-$) and 1,5-diynes ($-C\equiv C-CH_2CH_2-C\equiv C-$) undergo ready prototropic rearrangement on being treated with potassium *t*-butoxide in *t*-butyl alcohol, to yield, respectively, the corresponding conjugated trienes and dienynes.[4] A combination of these reactions appeared to provide a route to fully conjugated monocyclic large-ring systems and this objective has now been realized.

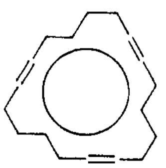
Cycloöctadeca-1,3,7,9,13,15-hexayne (I) (obtained in *ca.* 6% yield by the oxidation of 1,5-hexadiyne with cupric acetate in pyridine)[4] on treatment with potassium *t*-butoxide in *t*-butyl alcohol at 90° for 25 minutes rearranged in *ca.* 50% yield to a new substance, $C_{18}H_{12}$, which after chromatography on alumina crystallized from pentane as large brown plates, m.p. 190–192° (dec.; sample placed on block at 185°) (found: C, 94.71; H, 5.06). This substance is assigned the fully conjugated unstrained planar structure II [cycloöctadeca-1,7,13-(*cis*)-triene-3,9,15-(*trans*)-triene-5,11,-17-triyne],[5] derived from I by prototropic rearrangement of each 1,5-diyne to a 1,3-dien-5-yne unit. This structure follows from its properties as well as from an alternative method of preparation.[6]



I



II



IIa

The ultraviolet spectrum in isoöctane showed maxima at 245, 254, 322, 334, 365, 385, 400 and 434 mμ (ϵ = 18,800, 14,700, 98,000, 160,000, 8,700, 11,700, 15,200 and 1,080) and in benzene at 329, 342, 391, 407 and 441 mμ (ϵ = 95,000, 155,000, 12,000, 15,200 and 1,100). The infrared spectrum (KBr) showed bands at 3.30(w), 4.63(w), 4.75(w), 7.06(w), 7.78(m), 8.19(w), 8.40(w), 9.06(w), 10.32(s), 10.81(s), 11.86(s) and 13.20(s) μ. Hydrogenation in dioxane over platinum yielded cycloöctadecane, m.p. and mixed m.p. 72–73°, showing that no transannular reaction had occurred during the rearrangement.

The hexaene-triyne II contains a continuous molecular orbital and may be written as IIa.[7] It contains 18 π-electrons in conjugation and is the first conjugated monocyclic system known with more than the classical sextet. The substance complies with Hückel's rule for aromatic stability in cyclic molecular orbitals [presence of $(4n + 2)$ conjugated π-electrons],[8] although the carbon-carbon bonds are of course not all equivalent as would be required for maximum stability. As expected, II is a reasonably stable compound as judged by its method of formation in satisfactory yield, the exhibition of a melting point (with decomposition) near 200°, the fact that it can be kept with little change for several days at room temperature in light and air, etc.

In practice it was found most convenient to carry out the oxidation of 1,5-hexadiyne as before,[1] rearrange the total reaction product with potassium *t*-butoxide and chromatograph. In this way 0.41 g. of pure II was obtained simply from 15 g. of 1,5-hexadiyne. In addition other colored conjugated hydrocarbons were formed, the structures of which are being investigated.

We are grateful to Prof. R. B. Woodward and the late Prof. W. E. Moffitt for valuable discussions.

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[1] Part V, see F. Sondheimer, Y. Amiel and R. Wolovsky, THIS JOURNAL, **79**, 4247 (1957).

[2] F. Sondheimer, Y. Amiel and R. Wolovsky, *ibid.*, **78**, 4178 (1956); **79**, 4247, 5817, 6263 (1957); *Proc. Chem. Soc.*, 22 (1957).

[3] G. Eglinton and A. R. Galbraith, *Chem. and Ind.*, 737 (1956); *Proc. Chem. Soc.*, 350 (1957).

[4] *Cf.* E. R. H. Jones, M. C. Whiting, *et al.*, *J. Chem. Soc.*, 3197, 3201, 3208, 3212 (1954).

[5] For a discussion, but not the realization, of syntheses of related cyclic planar conjugated vinylacetylenes, see T. J. Sworski, *J. Chem. Phys.*, **16**, 550 (1948).

[6] F. Sondheimer, Y. Amiel and Y. Gaoni, THIS JOURNAL, **81**, 1771 (1959).

[7] *Cf.* W. von E. Doering and L. H. Knox, *ibid.*, **74**, 5683 (1952).

[8] E. Hückel, *Z. Physik*, **70**, 204 (1931); "Grundzüge der Theorie ungesättigter und aromatischer Verbindungen," Verlag Chemie, Berlin, 1938.

DANIEL SIEFF RESEARCH INSTITUTE
WEIZMANN INSTITUTE OF SCIENCE
REHOVOTH, ISRAEL
FRANZ SONDHEIMER
REUVEN WOLOVSKY

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UNSATURATED MACROCYCLIC COMPOUNDS. VII.[1] SYNTHESIS OF CYCLOÖCTADECA-1,3,7,9,13,15-HEXAENE-5,11,17-TRIYNE FROM 1,5-HEXADIYN-3-OL

Sir:

It has been shown recently that macrocyclic polyacetylenes can be prepared simply by the oxidative coupling of certain terminal diacetylenes.[2] A possible approach to the synthesis of completely conjugated macrocyclic unsaturated compounds involved the coupling of the hitherto unknown 1,5-hexadiyn-3-ol (I) and subjecting any

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[1] Part VI, F. Sondheimer and R. Wolovsky, THIS JOURNAL, **81**• 1771 (1959).

[2] F. Sondheimer, Y. Amiel and R. Wolovsky, *ibid.*, **78**, 4178 (1956); **79**, 4247, 5817, 6263 (1957); G. Eglinton and A. R. Galbraith, *Chem. and Ind.*, 737 (1956); *Proc. Chem. Soc.*, 350 (1957).