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THE SYNTHESIS OF CYCLOÖCTADECANONAENE, A NEW AROMATIC SYSTEM [*]

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THE synthesis and possible aromatic properties of monocyclic hydrocarbons formally containing alternating single and double bonds (vinylogs of benzene) have often been discussed.[1] Nevertheless the only member of this series known up to now besides benzene itself is cycloöctatetraene, despite numerous synthetic attempts to prepare other members. We now describe the synthesis of cycloöctadecanonaene (II) (for brevity named CON in this communication), the first cyclic polyene after benzene which might be expected to exhibit aromatic properties since (a) it can probably take up a planar or near planar configuration and (b) it

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[*] First presented at a Seminar at Harvard University, Nov. 21, 1958. This is Part IX of the Series, "Unsaturated Macrocyclic Compounds"; for Part VIII, see F. Sondheimer, Y. Amiel and R. Wolovsky, J. Amer. Chem. Soc. In press.

[1] Inter al. K. Mislow, J. Chem. Phys. **20**, 1489 (1952); W. Baker and J.F.W. McOmie in Progress in Organic Chemistry (Edited by J.W. Cook) Vol. 3, p. 44. Butterworths Scientific Publications, London (1955); W. Baker in Perspectives in Organic Chemistry (Edited by Sir A. Todd) p. 28. Interscience, New York (1956).

contains (4n + 2) π -electrons.[2]

We have recently reported two different syntheses of cycloöctadeca-1,7,13-(*cis*)-triene-3,9,15-(*trans*)-triene-5,11,17-triyne (I).[3,4] This compound on being partially hydrogenated in benzene over a "Lindlar" palladium catalyst[5] directly yielded a solution with three new ultra-violet maxima at 378, 415 and 456 mμ. Chromatograpny on alumina gave first unchanged I and then ca. 30% of CON (II) as long brown-red needles from chloroform (yellow-green solution in benzene), empirical formula $C_{18}H_{18}$ (found C, 91.76; H, 7.67), λisooctane 278,369, 408 and 448 mμ (ϵ = 8100, 303,000, 7500 and 21,800, $\lambda^{\text{benzene}}_{\text{max.}}$ 378, 415 and 456 mμ (ϵ = 297,000, 8700 and 28,400). In the infra-red (KBr) CON showed bands at 3.32 (m), 6.33 (w), 7.63(s), 7.93(m), 9.72(w), 10.36(m), 10.72(s), 11.86(s) and 13.16(w) μ. Full hydrogenation in diozane over platinum smoothly yielded cycloöctadecane, m.p. and mixed m.p. 72-73°.

The ultra-violet spectrum of CON indicates all the double bonds to be part of one chromophoric system (*cf.* the linear nonaene analog III, which has the highest wavelength maximum at 456 mμ, in benzene).[6]

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

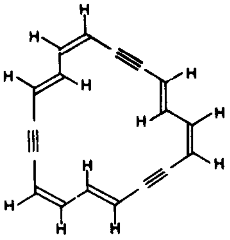
[3] F. Sondheimer and R. Wolovsky, *J. Amer. Chem. Soc.* In press.

[4] F. Sondheimer, Y. Amiel and Y. Gaoni, *J. Amer. Chem. Soc.* In press.

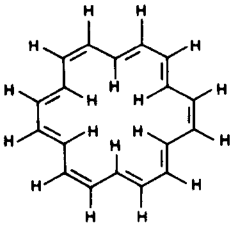
[5] H. Lindlar, Helv. Chim. Acta **35**, 446 (1952).

[6] F. Bohlmann, *Ber.* **85**, 386 (1952).

CON is therefore comparatively planar and it follows that the hydrogenation of I has resulted in trans-addition of hydrogen, since the usual cis-addition would have given a nonaene which cannot be planar.



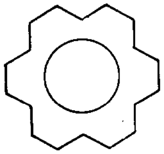
I



II

$Me-(CH=CH)_9-Me$

III



IIa

This view is substantiated by X-ray work now being carried out at this Institute by J. Bregman and G.M.J. Schmidt (to be published elsewhere); preliminary results based on the crystallographic constants suggest that CON is a near-planar molecule approximating to a centrosymmetric configuration.

CON contains a continuous molecular orbital and may be written as (IIa). It is an 18 π-electron system in which all the carbon-carbon bonds may well be equivalent and equal in length, as in benzene.[*]

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[*] We hope that a full X-ray structure analysis which is in progress will throw light on this important question.

CON shows definite aromatic character, being strikingly more stable than the acyclic analog III which decomposes very rapidly at room temperature.[6] Thus CON can be sublimed at 120-130° (0.5 mm) and on a Kofler block it appears to remain unchanged up to 230°.* However CON is not as stable as a classical benzenoid system (e.g. it gradually decomposes on being allowed to stand in light and air over the course of several weeks) and this may be a reflection of the interaction of the central hydrogen atoms.

Since the hexaene-triyne I is available in ca. 3% yield from 1,5-hexadiyne by a simple two-step route,[3] it is possible to prepare reasonable quantities of CON without undue difficulty. Various problems regarding the planarity and aromaticity of CON are now being investigated.

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* At this point a non-reversible colour-change takes place (the needles becoming light yellow without change of crystal shape), the nature of which is being studied.