diene" part of the C_8H_8 ring in a structural unit which is proving increasingly nearly general,[14,15,16,17] and which was suggested[18] for $C_4H_6Fe(CO)_3$, and employed[19] in interpreting closely related compounds and associated reactions. The structure also shows that six of the eight atoms of the ring are very nearly coplanar, and that six of the eight bond angles of the ring are within about 3° of the 135° angle of a completely regular and planar ring. The nature and extent of these distortions from the tub form of uncomplexed cyclooctatetraene make it possible that the $(COT)^-$ and $(COT)^{-2}$ ions may achieve planarity without great difficulty, as has long been anticipated from molecular orbital theory, and recently proposed[20,21] in connection with the preparation and properties of these ions, but distortions from planarity cannot yet be ruled out. Aside from these large bond angle distortions, the distances in the uncomplexed half of the ring in $C_8H_8Fe-(CO)_2$ are very suggestive of a butadiene residue, but a comparison of overlap integrals[22] which are 0.25 between C_4-C_5 or C_1-C_8 in $C_8H_8Fe(CO)_3$ and 0.04 between corresponding atoms in $(OC)_3-Fe(C_8H_8)Fe(CO)_3$, indicates that the butadiene halves of the C_8H_8 ring interact more strongly in $C_8H_8Fe(CO)_3$ than in $(OC)_3FeC_8H_8Fe(CO)_3$.

It is not known whether the equivalence of H^1 nuclear magnetic resonances, previously incorrectly attributed[13] to $(OC)_3FeC_8H_8Fe(CO)_3$, observed[1,2] for $C_8H_8Fe(CO)_3$ is indicative of negligible relative chemical shifts, a dynamical effect, or some difference of molecular geometry upon solution in carbon disulfide. A study of the temperature dependence of this spectrum may be of some help in elucidating this problem.

We wish to thank Dr. T. A. Manuel and Dr. F. G. A. Stone for their courtesy in supplying us with a sample, and we acknowledge support of this research by the Office of Naval Research.

(14) O. S. Mills and G. Robinson. *Proc. Chem. Soc. (London)*, 421 (1960).

(15) A. A. Hock and O. S. Mills, *Acta Cryst.*, **14**, 139 (1961).

(16) L. F. Dahl and D. L. Smith, private communication, 1961.

(17) R. E. Dodge and V. Schomaker, private communication, 1961.

(18) B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 642 (1958).

(19) R. B. Woodward, private communication, 1961.

(20) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784, 3785 (1960).

(21) T. J. Katz and H. L. Strauss, *J. Chem. Phys.*, **32**, 1873 (1960).

(22) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *ibid.*, **17**, 1248 (1949).

DEPARTMENT OF CHEMISTRY BRIAN DICKENS
HARVARD UNIVERSITY WILLIAM N. LIPSCOMB
CAMBRIDGE 38. MASS.
RECEIVED NOVEMBER 8. 1961

UNSATURATED MACROCYCLIC COMPOUNDS. XXIV.[1]
SYNTHESIS OF FOUR COMPLETELY CONJUGATED
SIXTEEN-MEMBERED RING CYCLIC SYSTEMS
Sir:

We have synthesized four completely conjugated sixteen-membered ring monocyclic hydrocarbons, namely, cyclohexadecaoctaene ([16]annulene[2]), cyclohexadecaheptaenyne (monodehydro[16]annulene[2]) and two isomers of cyclohexadeca-

(1) Part XXIII. F. Sondheimer, R. Wolovsky and Y. Amiel, *J. Am. Chem. Soc.*, in press.

(2) For the nomenclature employed, see Part XXI of this Series (F. Sondheimer and R. Wolovsky, *ibid.*, in press).

hexaenediyne (bis-dehydro[16]annulene[2]). These 16 π-electron systems were expected to be non-aromatic, since they do not comply with Hückel's rule for aromaticity [presence of $(4n + 2)$ π-electrons].

Reaction of *trans*-1,4-dibromo-2-butene with an excess of ethynylmagnesium bromide in tetrahydrofuran in the presence of cuprous chloride yielded besides other products[3] *ca.* 25% of *trans*-4-octene-1,7-diyne (I) [m.p. 15°, b.p. 59–60° (25 mm.), n^{19}D 1.4718; C_8H_8 (found: C, 92.28; H, 7.80; act. H, 2.01); no high-intensity absorption
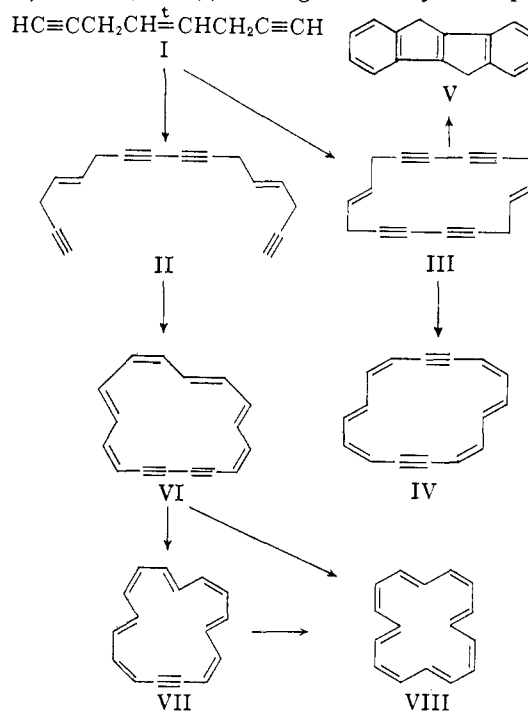
in the ultraviolet]. Coupling of I by passing oxygen into a mixture containing this hydrocarbon, ammonium chloride, cuprous chloride, ethanol and dilute hydrochloric acid[4] at 55° for 80 minutes produced *ca.* 25% of the linear dimer *trans-trans*-4,12-hexadecadiene-1,7,9,15-tetrayne (II) [colorless plates, m.p. 79–80°; $C_{16}H_{14}$ (found: C, 93.29; H, 6.79); $\lambda_{max}^{isooctane}$ 225, 239 and 253 mμ (ϵ 430, 390 and 240); converted by full hydrogenation to *n*-hexadecane, m.p. and mixed m.p. 17→18°] and 3 per cent. of the cyclic dimer *trans-trans*-1,9-cyclohexadecadiene-4,6,12,14-tetrayne (III) [colorless plates decomposing explosively at *ca.* 215°; $C_{16}H_{12}$ (found: C, 94.44; H, 5.96); λ_{max}^{ether} 232, 245 and 258 mμ (ϵ 740, 780 and 490); no terminal acetylene (infrared); converted by full hydrogenation to cyclohexadecane, m.p. and mixed m.p. 61–62°].

Treatment of the cyclic dimer III in benzene with a saturated solution of potassium *t*-butoxide in *t*-butyl alcohol at 40° for 1 minute yielded an isomeric mixture of bisdehydro[16]annulenes, chromatography on alumina giving violet and then orange solutions with main ultraviolet maxima

(3) See F. Sondheimer and Y. Gaoni, *ibid.*, **82**, 5765 (1960); **83**, 1259 (1961).

(4) See F. Sondheimer, *et al.*, *ibid.*, **79**, 5817, 6263 (1957); **81**, 6301 (1959).

in the 278–291 mμ region. One pure isomer, assigned the 1,7-diyne structure IV or a stereoisomeric one for symmetry reasons, could be isolated in *ca.* 5% yield as very unstable dark-brown plates (red-brown in solution), m.p. 59–60° dec. (sample placed on block just before); $\lambda_{max}^{isooctane}$ 279 and 290 mμ (ϵ 49,500 and 51,000) with absorption beyond 600 mμ; acetylene band at 4.58 μ in the infrared (chloroform). The monocyclic nature of the substance was demonstrated by full hydrogenation to cyclohexadecane. In addition, the reaction of III with potassium *t*-butoxide produced at least 15% of 10-diphenylsuccindene (V)[5] [slightly yellow plates, m.p. 212–213°; $\lambda_{max}^{isooctane}$ 230, 236, 243, 303, 314, 323 and 330 mμ (ϵ 12,800, 14,700, 12,000, 24,500, 28,800, 20,800 and 17,800)], identified with an authentic sample kindly provided by Prof. Fieser. This transannular reaction product was formed in over 50% yield when III was treated with boiling ethanolic potassium hydroxide.

Coupling of the linear dimer II (1 part) with cupric acetate (5 parts) in pyridine (300 parts) and ether (300 parts)[6,7] at 55° for 3.5 hr. yielded (besides other substances) *ca.* 1.5% of another bisdehydro[16]annulene, as well as material with main ultraviolet maxima at 362 and 392 mμ which was also formed by treatment of II with potassium *t*-butoxide in *t*-butyl alcohol and presumably consists of conjugated hexadecahexaenediyne(s). The new bisdehydro[16]annulene formed dark-brown needles (red in solution), m.p. 79–80° dec. (sample placed on block just before); $C_{16}H_{12}$ (found: C, 94.13; H, 5.67); $\lambda_{max}^{isooctane}$ 273, 279 and 290 mμ (ϵ 61,500, 63,500 and 43,500) with absorption beyond 600 mμ; acetylene band at 4.60 μ in the infrared (chloroform); converted by full hydrogenation to cyclohexadecane. The substance was very unstable, *e.g.*, it was almost completely decomposed after 15 minutes' standing in air and day-light, and detonated with a flash of fire on being rubbed with a spatula.

The last-described bisdehydro[16]annulene could not have been formed from II *via* III, since the latter was unaffected on being subjected to the reaction conditions which had given the conjugated substance. We believe the latter most probably to contain a 1,3-diyne grouping (VI or a stereoisomer), formed from II by rearrangement to hexadeca-3,5,7,9,11,13-hexaene-1,15-diyne(s) followed by oxidative ring-closure (or possibly by partial rearrangement of II, followed by ring-closure and further rearrangement). This type of pathway is supported by the formation of a considerable amount of conjugated hexadecahexaenediyne(s) in the reaction.

Partial hydrogenation of the last-mentioned bisdehydro[16]annulene in benzene over a "Lindlar" palladium catalyst yielded *ca.* 30% of a monodehydro[16]annulene (VII or a stereoisomer) as large brown plates (red-brown in solution), m.p.

(5) K. Brand and K. O. Müller, *Ber.*, **55**, 601 (1922); L. F. Fieser and M. M. Pechet, *J. Am. Chem. Soc.*, **68**, 2577 (1946).

(6) *Inter al.*, see G. Eglinton and A. R. Galbraith, *J. Chem. Soc.*, 889 (1959); F. Sondheimer, Y. Amiel and R. Wolovsky, *J. Am. Chem. Soc.*, **81**, 4600 (1959).

(7) It is to be noted that the coupling of the monomer I with cupric acetate in pyridine yielded a variety of cyclic and linear products (to be reported in the full paper), but no cyclohexadecane derivatives.

86–87°; $C_{16}H_{14}$ (found: C, 93.06; H, 6.71); $\lambda_{max}^{isooctane}$ 283 and 296 mμ (ϵ 52,000 and 41,000) with absorption beyond 600 mμ; acetylene band at 4.65 μ in the infrared (KBr). The compound proved to be considerably more stable than its precursor, showing a normal m.p. and suffering only *ca.* 30% decomposition after being allowed to stand for 4 days in air and daylight. This hydrogenation in addition produced in low yield a less polar substance as an orange oil, to which we assign the [16]annulene structure (VIII or a stereoisomer) in view of the ultraviolet spectrum $\lambda_{max}^{isooctane}$ 282 and 353 mμ (ϵ 44,500 and 3,500)] and the infrared spectrum (absence of acetylene band in the 4.5–4.7 μ region). Apparently the same [16]annulene was formed by the partial hydrogenation of the monodehydro[16]annulene, as evidenced by the essentially identical ultraviolet spectra and chromatographic behavior. [16]-Annulene was unstable and soon decomposed on standing, either neat or in solution.

DANIEL SIEFF RESEARCH INSTITUTE FRANZ SONDHEIMER
WEIZMANN INSTITUTE OF SCIENCE
REHOVOTH, ISRAEL YEHIEL GAONI

THE PREPARATION OF *trans* 1,4-POLYBUTADIENE BY RHODIUM SALTS IN SOLUTION

Sir:

We wish to report the preparation of crystalline *trans*-1,4-polybutadiene by the catalytic action of solutions of Rh^{+++} salts on butadiene monomer. Water, ethanol, and dimethylformamide were used as typical solvents. Representative polymerization conditions are summarized in Table I. The polymer was gel free in hot xylene. Because of its high crystallinity, it was not soluble in cold benzene. Under the conditions listed, polymer was obtained which had intrinsic viscosities of 0.1 to 0.5 in tetralin at 135°. Intrinsic viscosities as high as 1.0 were obtained by running the polymerization in emulsion at low temperature, and at very low rhodium concentrations. Increasing the temperature or the rhodium concentration decreased the molecular weight of the polymer.

The fastest rates were observed when the reactions were carried out in water with a suitable emulsifier such as sodium lauryl sulfate or sodium dodecylbenzene sulfonate. There was no evidence of an induction period. The presence of hydroquinone or air did not reduce the rate.

All the Rh^{+++} salts listed in Table I were active catalysts, although some were effective under conditions in which others were ineffective. Thus, $RhCl_3$ produced no noticeable *trans*-polybutadiene after six hours at 80° in alcohol, whereas 1 g. of $Rh(NO_3)_3$ produced about 7 g. of polymer per hour under the same conditions. A solution of the nitrate in 95% ethanol saturated with butadiene gave crystalline polymer in an open flask in the atmosphere at room temperature. After one day, the polymer was removed by filtration, and was washed with more ethanol. The filtrate and combined washings were concentrated to about the original volume, and more butadiene was added. Polymerization occurred as before. The slightly slower rate could be attributed to loss of rhodium