nitrogen species (NH).[6] The intermediates at the end stages of the reaction are also of more general interest because of their similarity to those in Wolff–Kishner reductions,[7] and also because of current interest in the mechanisms of electrophilic substitutions on carbon.[8]

TABLE I

	Amine	Sulfonamide derivative[a]	Yield of hydrocarbon, % Actual	Corrected
1	Benzylamine	Bs	63	>95
2(i)	α-Phenylethylamine	Ms[b]	60	81
(ii)	α-Phenylethylamine	Ms[b]	81[c]	86
3(i)	2-Phenyl-2-butylamine	Bs	10	>95
(ii)	2-Phenyl-2-butylamine	Bs	33[d]	>95
4	*n*-Hexylamine	Ts	41	>95
5	2-Octylamine	Ts	17	93
6	2,4,4-Trimethyl-2-pentylamine	Ts	12	>95
7	Cyclohexylamine	Bs	23	72
8	9-Amino-9,10-ethano-9,10-dihydroanthracene	Ms	6	81
9	β-Naphthylamine	Ts[b]	19	[e]

[a] Bs = benzenesulfonamide; Ts = toluenesulfonamide; Ms = methanesulfonamide. [b] Ethanol omitted from alkaline solution. [c] 45 equivalents of reagent used; product removed by five successive distillations, each conducted after 20% of the reagent had been added. [d] 50 equivalents of reagent, with a distillation conducted midway as well as at the end. [e] Not determined.

$$\begin{tikzcd}
RNHSO_2R' \arrow[r, "\text{Over-all}"] \arrow[d, "{}^{-}OH"', "NH_2OSO_3^{-}"] & RH \\
\begin{matrix} RNNH_2 \\ | \\ SO_2R' \end{matrix} \arrow[r, "-R'SO_2H"] & RN{=}NH \arrow[u, "-N_2"']
\end{tikzcd}$$

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(6) A. Meuwsen and R. Gösl, *Angew. Chem.*, **69**, 754 (1957).

(7) D. Todd, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., Vol. IV, 1948, p. 378; R. B. Turner, R. Anliker, R. Helbling, J. Meier and H. Heusser. *Helv. Chim. Acta*, **38**, 411 (1955); N. J. Leonard and S. Gelfand, THIS JOURNAL, **77**, 3272 (1955); G. Lardelli and O. Jeger, *Helv. Chim. Acta*, **32**, 1817 (1949).

(8) D. J. Cram, *et al.*, THIS JOURNAL, **81**, 5740–5785 (1959).

(9) This work was supported by a Frederick Gardner Cottrell grant from Research Corporation, and by the Alfred P. Sloan Foundation.

(10) Alfred P. Sloan Foundation Fellow.

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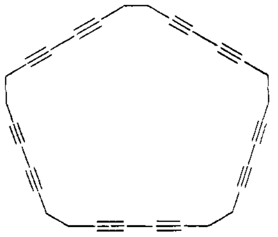
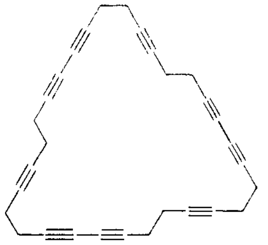
UNSATURATED MACROCYCLIC COMPOUNDS. XII.[1] SYNTHESIS OF TWO COMPLETELY CONJUGATED THIRTY-MEMBERED RING CYCLIC SYSTEMS

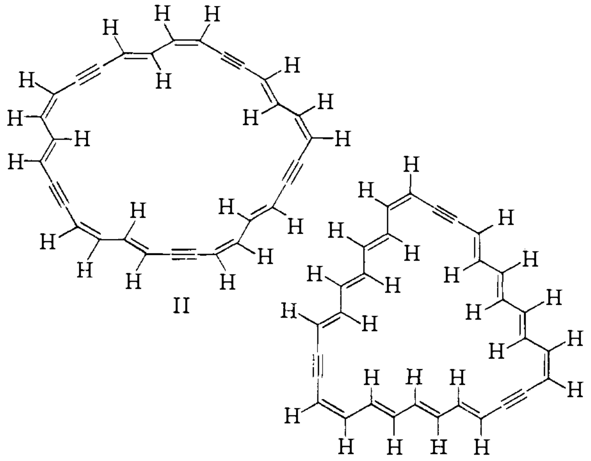
Sir:

We have prepared cyclotriaconta-1,3,7,9,13,15,19,21,25,27-decaene-5,11,17,23,29-pentayne (II or a stereoisomer) and cyclotriaconta-1,3,5,7,11,13,15,17,21,23,25,27-dodecaene-9,19,29-triyne (IV or a stereoisomer), completely conjugated thirty-membered ring cyclic polyene-ynes containing five and three acetylenic bonds, respectively. These represent the first monocyclic conjugated 30 π-electron systems and they comply with Hückel's rule for aromaticity [presence of (4*n* + 2) π-electrons].

The first substance was obtained in *ca.* 20% yield from cyclotriaconta-1,3,7,9,13,15,19,21,25,27-decayne (I) (the cyclic "pentamer" of 1,5-hexadiyne)[2] by treatment with potassium *t*-butoxide in *t*-butyl alcohol–benzene at 90° for 30 minutes. The resulting isomer (found: C, 94.18; H, 5.42) formed orange-red crystals from ether (red in solution), which decomposed when heated; $\lambda_{\max}^{\text{dioxane}}$ (principal bands) 307, 318, 378 and 396 mμ (ε = 42,000, 39,500, 105,000 and 126,000); $\lambda_{\max}^{\text{benzene}}$ (principal bands) 310, 320, 383 and 400 mμ (ε = 38,000, 35,500, 101,000 and 122,000). The infrared spectrum (KBr) showed bands at 3.31 μ (—CH=), 4.64 μ (—C≡C—), 7.11 μ (*cis*-double bond), 7.77 and 10.34 μ (*trans*-double bond). Full hydrogenation (platinum, dioxane) gave cyclotriacontane,


I


III



II

IV

m.p. and mixed m.p. 55–57°. The rearrangement doubtless took place analogously to that of the cyclic "trimer"[3] and "tetramer"[1] of 1,5-hexadiyne to give a fully conjugated decaene-pentayne, and the product is most probably the symmetrical 1,7,13,19,25-pentayne (II or a stereoisomer).

The second conjugated substance was prepared in this way. Reaction of *trans*-1,4-dibromo-2-butene with allylmagnesium bromide at 5° gave *ca.* 50% of *trans*-1,5,9-decatriene [b.p. 69–70° (18 mm.), n^{25}D 1.4432; found: C, 87.82; H, 11.63], which on conversion to the hexabromide (mixture of isomers) and subsequent dehydrobromination with sodamide in liquid ammonia[4] yielded *ca.* 25% of 1,5,9-decatriyne [m.p. 46°, b.p. 61–63° (2 mm.); found: C, 91.82; H, 7.66]. Oxidation with cupric acetate in pyridine[2,5] at

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(1) Part XI, see F. Sondheimer and R. Wolovsky, THIS JOURNAL, **81**, 4755 (1959).

(2) F. Sondheimer, Y. Amiel and R. Wolovsky, *ibid.*, **79**, 4247 (1957).

(3) F. Sondheimer and R. Wolovsky, *ibid.*, **81**, 1771 (1959).

(4) See R. A. Raphael and F. Sondheimer, *J. Chem. Soc.*, 120 (1950).

(5) See G. Eglinton and A. R. Galbraith, *Chemistry & Industry*, 737 (1956); *J. Chem. Soc.*, 889 (1959); F. Sondheimer, Y. Amiel and R. Wolovsky, THIS JOURNAL, **81**, 4600 (1959).

55° for 4 hr. gave (besides other products) *ca.* 5% of the cyclic "trimer", cyclotriaconta-1,3,7,11,-13,17,21,23,27-nonayne (III) [m.p. 198–199° dec.; $\lambda_{\max}^{\text{isoöctane}}$ 226,234 and 255 mμ; found: C, 93.68; H, 6.27]; full hydrogenation (platinum, dioxane) yielded cyclotriacontane, m.p. and mixed m.p. 56–57°.

Rearrangement of III with potassium *t*-butoxide in *t*-butyl alcohol–benzene[1,3] at 90° for 20 minutes led to *ca.* 20% of an isomer, dark brown-violet crystals from pentane-ether (red in solution), which decomposed when heated; $\lambda_{\max}^{\text{dioxane}}$ 320 and 401 mμ (ϵ = 51,000 and 113,000); $\lambda_{\max}^{\text{benzene}}$ 323 and 406 mμ (ϵ = 47,000 and 108,000). The infrared spectrum (KBr) showed bands at 3.31 μ (—CH=), 4.64 μ (—C≡C—), 7.09 μ (*cis*-double bond), 7.76 and 10.33 μ (*trans*-double bond). Full hydrogenation (platinum, dioxane) gave cyclotriacontane, m.p. and mixed m.p. 57–58°. The rearrangement product is clearly a fully conjugated dodecaene-triyne and a symmetrical 1,11,21-triyne structure (IV or a stereoisomer) appears most probable.

Both the fully conjugated systems described are reasonably stable and can be kept with little change in light and air for 24 hr. in the solid state or for several weeks in dilute benzene solution.

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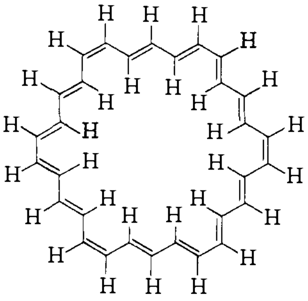
RECEIVED DECEMBER 19, 1959

UNSATURATED MACROCYCLIC COMPOUNDS. XIII.[1] CYCLOTRIACONTAPENTADECAENE

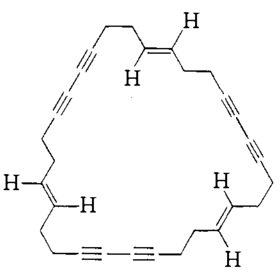
Sir:

Cyclotriacontapentadecaene (CTP) (I) is a fully conjugated cyclic polyene which was expected to exhibit aromatic character, since it contains ($4n + 2$) π-electrons ($n = 7$) and it probably can exist in a planar configuration. In fact CTP has been postulated as the smallest conjugated cyclic polyene with aromatic properties,[2] as the degree of proximity which exists between *every* "internal" hydrogen atom in cycloöctadecanonaene[3] exists only between every *alternate* "internal" hydrogen atom in CTP. We now describe two syntheses of CTP and experiments which indicate that in fact this does not represent a stable system.

Cyclotriacontadecaenepentayne (formula II or stereoisomer in the preceding Communication)[1] in benzene was allowed to absorb 5 moles of hydrogen over a "Lindlar" palladium catalyst. Chromatography on alumina first gave starting material and then *ca.* 5% of a substance, dark brown-red crystals from ether, which decomposed on heating; $\lambda_{\max}^{\text{dioxane}}$ 329 and 428 mμ (ϵ = 44,000 and 144,000); $\lambda_{\max}^{\text{benzene}}$ 331 and 432 mμ (ϵ = 43,000 and 140,000). The infrared spectrum (KBr) no longer showed the acetylene band at 4.64 μ. Although the new compound was too unstable for accurate elemental analysis, the results obtained with two different samples (found: C, 88.82, 88.52; H, 7.36, 7.52) indicated a $C_{30}H_{30}$ formula (C:H ratio = 30:29.6; 30:30.4). Full hydrogenation (platinum. dioxane) gave cyclotriacontane, m.p. and mixed m.p. 56–57°.



I



III

$$\text{H-(-C}{\equiv}\text{CCH}_2\text{CH}_2\text{CH}\overset{t}{=}\text{CHCH}_2\text{CH}_2\text{C}{\equiv}\text{C—)}_n\text{-H}$$

IIa, $n = 1$
b, $n = 2$

The data show the partial hydrogenation product to be a CTP. Although it is not known with certainty whether it is the 1,11,21-tri-(*cis*)-ene (I) or a stereoisomer, evidence for structure I is provided by the fact that the same substance is obtained (as indicated by the identical ultraviolet spectrum and chromatographic behavior) in *ca.* 10% yield through the addition of 3 moles of hydrogen to cyclotriacontadodecaenetriyne (formula IV or stereoisomer in the preceding Communication)[1] in benzene over a Lindlar catalyst.

The synthetic CTP is unstable, being destroyed by standing in light and air for several hours or attempted isomerization with a trace of iodine in boiling benzene; it also gradually decomposes in dilute benzene or dioxane solution at room temperature.

Although the possibility exists that the instability of the synthetic CTP is due to it being a stereoisomer of I which is not planar, the series of experiments reported provides independent evidence that I is not an aromatic system.

Reaction of *trans*-1,4-dibromo-2-butene with allenylmagnesium bromide (from propargyl bromide, magnesium and mercuric chloride)[4] catalyzed with cuprous chloride gave *ca.* 50% of *trans*-5-decene-1,9-diyne (IIa) [b.p. 81–82° (20 mm.), n^{19}D 1.4701; found: C, 90.55; H, 9.12; act. H, 1.50]. Oxidation with cupric acetate in pyridine at 65° for 3.5 hr. yielded (besides other products) *ca.* 2.5% of the cyclic trimer, cyclotriaconta-1,11,21-tri-(*trans*)-ene-5,7,15,17,25,27-hexayne (III) (m.p. 111–112°; $\lambda_{\max}^{\text{isooctane}}$ 226, 240 and 254 mμ; found: C, 91.59; H, 7.54). Full hydrogenation (platinum, dioxane) led to cyclotriacontane, m.p. and mixed m.p. 57–58°.

Attempted isomerization of III with potassium *t*-butoxide in *t*-butyl alcohol–benzene at 90°, then careful chromatography on alumina, gave no indication that a conjugated CTP of type I had been formed in reasonable yield. On the other hand, the same conditions resulted in the isomerization of the monomer IIa to 1,3,5,7,9-decapentaene (15% yield; m.p. 145–147° dec.; $\lambda_{\max}^{\text{isooctane}}$ 291, 303, 317 and 334 mμ)[5] and of the linear dimer IIb (m.p. 57°) to

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[1] Part XII, see F. Sondheimer, R. Wolovsky and Y. Gaoni, THIS JOURNAL, **82**, 754 (1960).

[2] K. Mislow, *J. Chem. Phys.*, **20**, 1489 (1952).

[3] F. Sondheimer and R. Wolovsky, *Tetrahedron Letters*, No. 3, 3 (1959).

[4] See M. Gaudemar, *Ann. chim.* (*Paris*), (1) **13**, 190 (1956) C. Prévost, M. Gaudemar, L. Miginiac, F. Bardone-Gaudemar and M. Andrac, *Bull. soc. chim. France*, 679 (1959).

[5] A. D. Mebane, THIS JOURNAL, **74**, 5227 (1952).