lized satisfactorily and gave poor carbon values, perhaps because of contamination by the ether XV which sometimes cannot be separated satisfactorily from the mesylate.

Anal. Calcd. for $C_{14}H_{18}O_3S$: C, 63.14; H, 6.81; S, 12.20. Found: C, 64.95; H, 6.99; S, 11.75.

exo-**1-Methyl-2,3-benzbicyclo(3,2,1)-4-octanol (VIII).**—A solution of unpurified mesylate, prepared from 5 g. of alcohol VIIa, in wet benzene–petroleum ether was chromatographed over basic alumina. Elution with diethyl ether yielded crystalline material which was recrystallized from ligroin; total yield of once-recrystallized material 2.7 g. (54%), m.p. 80–82°.

Anal. Calcd. for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 83.14; H, 8.79.

A solution of 1.09 g. of mesylate, previously chromatographed over acid-washed alumina using anhydrous solvents was chromatographed over basic alumina. Benzene–petroleum ether eluted 0.190 g. of a non-polar fraction which was recrystallized from ethanol, m.p. 165–168°, and shown to be the ether XV by infrared (no hydroxyl or mesylate bands) and n.m.r. spectrum (benzene resonance at 7.15, doublet at 4.38, $J = 2$, –CH–O–, complex band system for methylene and methine protons, and 1.47 p.p.m., (C_1–methyl).

Anal. Calcd. for $C_{26}H_{30}O$: C, 87.10; H, 8.44; O, 4.46. Found: C, 87.24; H, 8.27; O, 4.59.

Elution with diethyl ether resulted in recovery of 0.725 g. of mesylate.

1-Methyl-2,3-benzbicyclo(3,2,1)-4-octanone (XI).—Oxidation of 1.5 g. of VIII with chromic oxide–pyridine complex[13] yielded after decomposition with ice, extraction with ether, washing, drying of the ether extract, 1.2 g. (80%) of XI, b.p. 91–93° (0.2 mm.), infrared band at 1680 cm.$^{-1}$, n.m.r. signals at 8.01 (1 proton, doublet of triplets, *peri*-hydrogen), 7.38 (3 protons, benzene resonance), 3.12 (1 proton, doublet of doublets), methylene and methine hydrogens (total intensity 6 protons) and 1.63 p.p.m. (C_1–methyl).

Anal. Calcd. for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.68; H, 7.60.

The dinitrophenylhydrazone, scarlet needles from ethanol–ethyl acetate, melted at 228–230°.

Anal. Calcd. for $C_{19}H_{18}N_4O_4$: C, 62.28; H, 4.95; N, 15.29. Found: C, 61.90; H, 4.96; N, 15.39.

The ketone XI was also prepared by desulfurization of 0.3 g. of the thioketal XIII with W-2 Raney nickel in absolute ethanol. The identity was established by conversion to the dinitrophenylhydrazone, m.p. and mixed m.p. and infrared spectra.

endo-**1-Methyl-2,3-benzbicyclo(3,2,1)-4-octanol (XIV).**—Reduction of 1 g. of XI with 1 g. of sodium borohydride in 95% ethanol in the usual fashion yielded, after hydrolysis, extraction with ether, drying and removal of solvent, material which was recrystallized from petroleum ether; m.p. 59–62°, yield 0.5 g., n.m.r. signals at 7.18 (4 protons, center of benzene resonance), 4.95 (1 proton, doublet, $J = 5$, H_4), 2.85 (–OH), 2.45 (1 proton, complex multiplet, H_5), 1.65 (6 protons, center of complex system, H_6, H_7 and H_8) and 1.37 p.p.m. (C_1–methyl).

Anal. Calcd. for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 83.59; H, 8.59.

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[13] G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE, THE WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL

Unsaturated Macrocyclic Compounds. XXV.[1] The Synthesis of Bisdehydro-[20]annulene,[2] [20]Annulene, Tridehydro-[30]annulene and [30]Annulene from 1,5,9-Decatriyne

BY FRANZ SONDHEIMER AND YEHIEL GAONI

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Two syntheses of 1,5,9-decatriyne (V) are described. The oxidative coupling of this triacetylene with cupric acetate in pyridine yielded the cyclic dimer IX and cyclic trimer XII, as well as the linear dimer VIIIa and linear tetramer VIIIb. The cyclic dimer IX was rearranged with potassium *t*-butoxide in *t*-butyl alcohol to bisdehydro-[20]annulene (*e.g.*, X), which was converted by partial hydrogenation to [20]annulene (*e.g.*, XI). Similarly, the cyclic trimer XII was rearranged to tridehydro-[30]annulene (*e.g.*, XIII), which on partial hydrogenation produced [30]annulene (*e.g.*, XIV).

It has been shown previously that the oxidative coupling of aliphatic α,ω-diacetylenes may give rise to large-ring polyacetylenes[3,4] and that linear 1,5-diacetylenes are rearranged by means of potassium *t*-butoxide to conjugated polyen-ynes.[5] In part XXI of this series[2] we described the use of a combination of both of these types of reactions for the synthesis of a number of fully conjugated macrocyclic polyene-polyynes (dehydro-annulenes), 1,5-hexadiyne being subjected to the coupling reaction, followed by prototropic rearrangement of the resulting cyclic products. An alternative route to large-ring polyacetylenes made up of 1,5-diyne units, suitable for rearrangement to dehydro-annulenes, appeared to involve the oxidative coupling of the hitherto unknown 1,5,9-decatriyne (V). In the present paper we report the synthesis of this compound,[6a] its coupling to the cyclic dimer IX[6c] and trimer XII,[6a] and the prototropic rearrangement of these substances[7] to bisdehydro-[20]annulene (*e.g.*, X)[6c] and tridehydro-[30]annulene (*e.g.*, XIII).[6a] These dehydro-annulenes were then converted by partial hydrogenation to [20]annulene (*e.g.*, XI)[6c] and [30]annulene (*e.g.*, XIV),[6b] respectively.

Two different syntheses of 1,5,9-decatriyne (V) were developed. The preferred method was modeled on the synthesis of 1,5-hexadiyne from

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[1] For Part XXIV, see F. Sondheimer and Y. Gaoni, *J. Am. Chem. Soc.*, **83**, 4863 (1961).

[2] For the nomenclature employed, see F. Sondheimer and R. Wolovsky, *ibid.*, **84**, 260 (1962).

[3] (a) F. Sondheimer and Y. Amiel, *ibid.*, **79**, 5817 (1957); (b) F. Sondheimer, Y. Amiel and R. Wolovsky, *ibid.*, **79**, 6263 (1957); (c) F. Sondheimer, Y. Amiel and R. Wolovsky, *ibid.*, **81**, 4600 (1959).

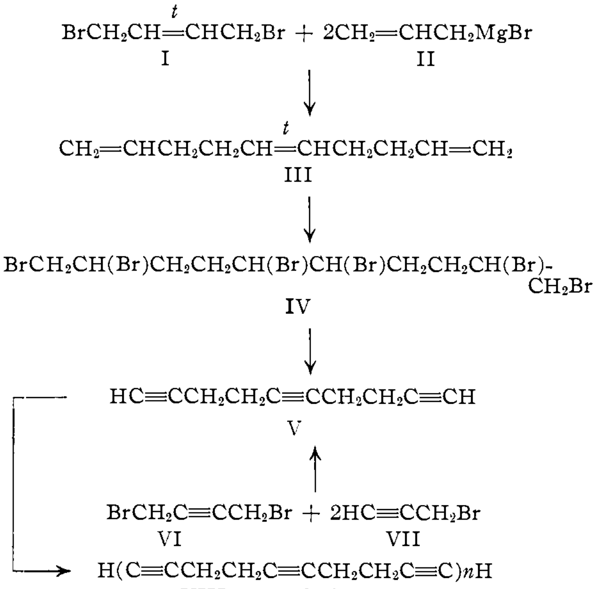
[4] G. Eglinton and A. R. Galbraith, *J. Chem. Soc.*, 889 (1959).

[5] F. Sondheimer, D. A. Ben-Efraim and Y. Gaoni, *J. Am. Chem. Soc.*, **83**, 1682 (1961).

[6] For preliminary communications, see (a) F. Sondheimer, R. Wolovsky and Y. Gaoni, *ibid.*, **82**, 754 (1960); (b) F. Sondheimer, R. Wolovsky and Y. Gaoni, *ibid.*, **82**, 755 (1960); (c) F. Sondheimer and Y. Gaoni, *ibid.*, **83**, 1259 (1961).

[7] The prototropic rearrangement of 1,5,9-decatriyne (V) itself with potassium *t*-butoxide has been described in part XVIII of this series.[5]

allyl chloride, through conversion to 1,5-hexadiene by means of magnesium,[8] followed by addition of bromine and subsequent dehydrobromination.[9] The starting material was *trans*-1,4-dibromo-2-butene (I),[10] which on reaction with allylmagnesium bromide (II)[11] yielded 50% of the liquid *trans*-1,5,9-decatriene (III). In keeping with the assigned structure, the triene III showed infrared bands at 6.09, 10.10 and 10.94 μ (monosubstituted ethylene)[12a] as well as at 10.33 μ (*trans*-disubstituted ethylene),[12a] and exhibited no appreciable absorption in the ultraviolet. Treatment with 3 molar equivalents of bromine in pentane or carbon tetrachloride solution converted III to 1,2,5,6,9,10-hexabromodecane (IV). Rather surprisingly, this reaction led mainly to a single isomer of the hexabromide, the yield of apparently pure product, m.p. 114–115°, being in the range 58–72%. The pure hexabromide was then dehydrobrominated with sodamide in liquid ammonia,[13] whereby the required 1,5,9-decatriyne (V), m.p. 46°, was obtained in *ca.* 25% yield. The structure of this triyne was confirmed by the presence of infrared bands at 3.03 and 4.70 μ due to the monosubstituted acetylene grouping[12b,14] (disubstituted acetylene bands in the 4.42–4.57 μ region could not be detected, presumably because of the symmetry of the molecule[12b,14]), and by the absence of appreciable absorption in the ultraviolet.



$$\underset{\text{I}}{BrCH_2\overset{t}{CH{=}CH}CH_2Br} + \underset{\text{II}}{2CH_2{=}CHCH_2MgBr}$$
$$\downarrow$$
$$\underset{\text{III}}{CH_2{=}CHCH_2CH_2\overset{t}{CH{=}CH}CH_2CH_2CH{=}CH_2}$$
$$\downarrow$$
$$\underset{\text{IV}}{BrCH_2CH(Br)CH_2CH_2CH(Br)CH(Br)CH_2CH_2CH(Br)\text{-}CH_2Br}$$
$$\downarrow$$
$$\underset{\text{V}}{HC{\equiv}CCH_2CH_2C{\equiv}CCH_2CH_2C{\equiv}CH}$$
$$\uparrow$$
$$\underset{\text{VI}}{BrCH_2C{\equiv}CCH_2Br} + \underset{\text{VII}}{2HC{\equiv}CCH_2Br}$$
$$\longrightarrow H(C{\equiv}CCH_2CH_2C{\equiv}CCH_2CH_2C{\equiv}C)_nH$$

VIIIa, $n = 2$; b, $n = 4$

The second synthesis of 1,5,9-decatriyne (V) involved the treatment of 1,4-dibromo-2-butyne (VI)[15] with the Grignard reagent prepared from propargyl bromide (VII) and magnesium (catalyzed with mercuric chloride).[16] Despite the fact that the analogous reaction between *trans*-1,4-dibromo-2-butene (I) and this Grignard reagent had yielded *trans*-5-decene-1,9-diyne in reasonable yield,[17] the present reaction gave only *ca.* 1.5% of the triyne V (identical with that obtained before) besides a considerable amount of allenic material. The first-mentioned route to V is therefore the preferred one.

1,5,9-Decatriyne (V) was submitted to oxidative coupling with cupric acetate in pyridine at 55° for 4 hr., the dilution (1 part of triyne in 100 parts of pyridine) being the same as used by us previously.[2,3c,17] Careful chromatography on alumina then yielded four different crystalline substances which proved to be, in order of elution, the linear dimer VIIIa (1.6%, m.p. 143–144°), the cyclic dimer IX (6.2%, m.p. 230–231° dec.), the cyclic trimer XII (5.2%, m.p. 198–199° dec.) and the linear tetramer VIIIb (1.9%, m.p. 192–194° dec.). In accord with the assigned structures, the cyclic compounds IX and XII showed infrared bands at 4.43 and 4.62 μ (α,γ-diacetylene)[3c] but none at *ca.* 3.00 or 4.70 μ due to terminal acetylene.[12b,14] Their ultraviolet spectra exhibited the medium intensity triplet at *ca.* 226, 237 and 255 mμ typical of the α,γ-diacetylene chromophore,[18] and full hydrogenation smoothly led to cycloeicosane and cyclotriacontane, respectively. The linear substances VIIIa and VIIIb in the infrared showed bands at 4.43 and 4.62 μ (α,γ-diacetylene)[3c] as well as at 3.03 and 4.71 μ (terminal acetylene),[12b,14] while full hydrogenation yielded *n*-eicosane and *n*-tetracontane, respectively.

Both the cyclic dimer IX and the cyclic trimer XII are made up of 1,5-diyne units, and should be convertible to the corresponding dehydro-annulenes by prototropic rearrangement.[5,7] In practice, the cyclic dimer IX in benzene on being boiled for 15 minutes with a saturated solution of potassium *t*-butoxide in *t*-butyl alcohol gave a red solution with a sharp new ultraviolet maximum at 320 mμ (in ether). Chromatography on alumina then led to a substance (spectroscopic yield, 27%; yield of crystalline product, 16%), the properties of which show it to be bisdehydro-[20]annulene (X or an isomer). This compound, which crystallized as regular dark brown-violet plates (m.p. 176–177° dec.), proved to be isomeric with the starting material IX. The ultraviolet spectrum, presented in Table I and Fig. 1, showed two maxima (at 319 and 336 mμ, in isoöctane) very close to the main maxima of tridehydro-[18]annulene (at 322 and 334 mμ, in isoöctane)[2,19] and of tetrahydro[24]-

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[8] A. Turk and H. Chanan, *Org. Syntheses*, **27**, 7 (1947).

[9] R. A. Raphael and F. Sondheimer, *J. Chem. Soc.*, 120 (1950), and references cited there.

[10] Prepared from butadiene and bromine, according to E. M. Shantz, *J. Am. Chem. Soc.*, **68**, 2553 (1946).

[11] O. Grummitt, E. P. Budewitz and C. C. Chudd, *Org. Syntheses*, **36**, 61 (1956).

[12] See L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1958; (a) Chapter 3; (b) Chapter 4.

[13] See T. H. Vaughn, R. R. Vogt and J. A. Nieuwland, *J. Am. Chem. Soc.*, **56**, 2120 (1934).

[14] J. H. Wotiz and F. A. Miller, *ibid.*, **71**, 3441 (1949).

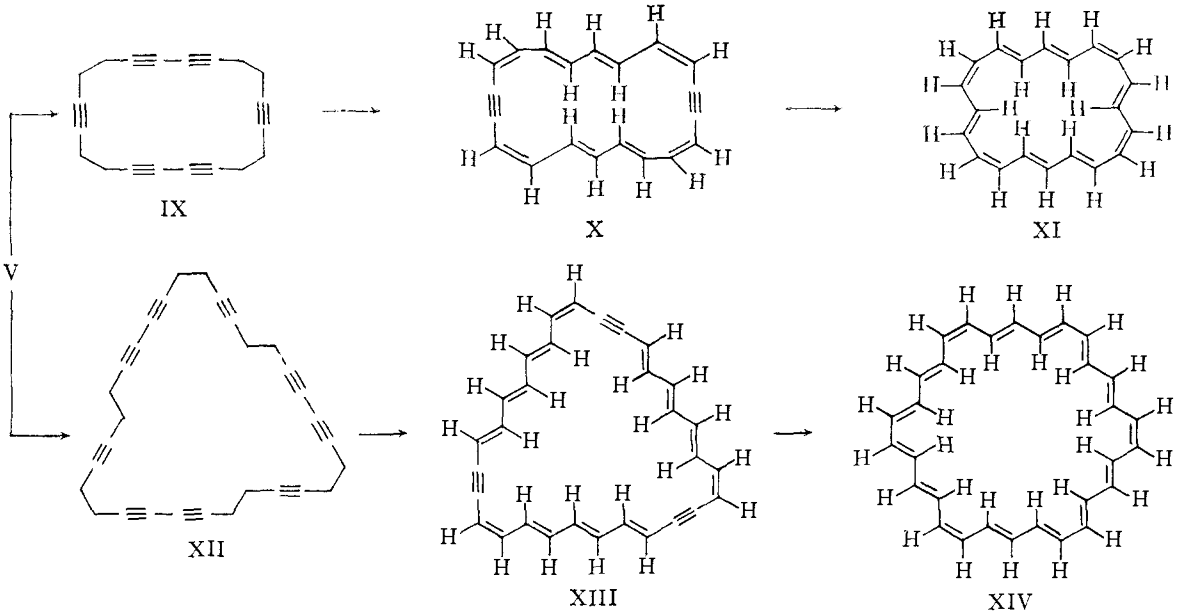
[15] Prepared from 2-butyne-1,4-diol as described by A. W. Johnson, *J. Chem. Soc.*, 1009 (1946).

[16] M. Gaudemar, *Ann. chim.* (*Paris*), [13] 1, 190 (1956). This reagent has been shown to exist in the allenic form (C. Prévost, M. Gaudemar, L. Miginiac, F. Bardone-Gaudemar and M. Andrac, *Bull. soc. chim. France*, 679 (1959); T. L. Jacobs and T. L. Moore, Abstracts of Papers, 141st Meeting of the American Chemical Society, Washington, D. C., March, 1962, p. 19-O).

[17] F. Sondheimer, R. Wolovsky and D. A. Ben-Efraim, *J. Am. Chem. Soc.*, **83**, 1686 (1961).

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

[19] F. Sondheimer, Y. Amiel and Y. Gaoni, *J. Am. Chem. Soc.*, **84**, 270 (1962).



annulene (at 324 and 340 mμ, in isoöctane).[2,20] The infrared spectrum showed an acetylene band at 4.64 μ,[12b] but no allene band in the 5.1 μ region.[12b] Full hydrogenation smoothly produced cycloeicosane, confirming that the isomerization product was still monocyclic. The two acetylenic bonds in bisdehydro-[20]annulene from symmetry considerations are placed in a 1,11-relationship as shown in X, but it is not possible at present to make any definite stereochemical assignments to the double bonds.

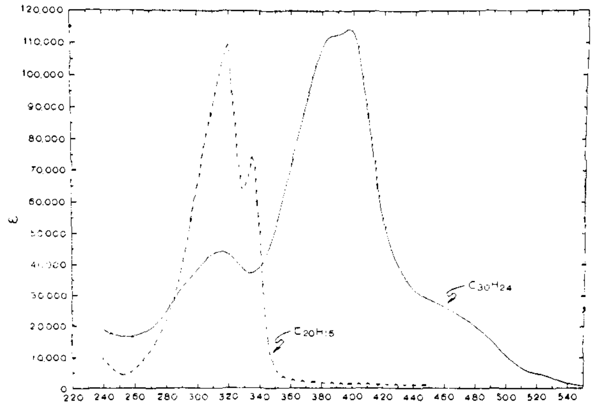


Fig. 1.—Ultraviolet absorption spectra (in isoöctane) of bisdehydro-[20]annulene ($C_{20}H_{16}$) and tridehydro-[30]-annulene ($C_{30}H_{24}$).

The cyclic trimer XII was rearranged similarly through being boiled in benzene for 20 minutes with a saturated solution of potassium *t*-butoxide in *t*-butyl alcohol, whereby a red solution with well-defined new ultraviolet maxima at 321 and 397 mμ (in benzene) was produced. Careful chromatography on alumina and subsequent crystallization then led to tridehydro-[30]annulene (XIII or an isomer) as dark brown-violet crystals which decomposed without melting on attempted melting point determination. The yield of rearranged substance was 19% determined spectroscopically, whereas 10% could be isolated in crystalline form. The ultraviolet spectrum of the tridehydro-[30]annulene is given in Table I and Fig. 1. In agreement with the assigned structure, the position of the main maximum (at 406 mμ, in benzene) is intermediate between that of pentadehydro-[30]-annulene (at 400 mμ, in benzene)[2] and that of [30]annulene (at 432 mμ, in benzene).[21] The infrared spectrum exhibited an acetylene band at 4.64 μ,[12b] but no allene bands. Full hydrogenation readily led to cyclotriacontane, showing that no transannular reaction had taken place.

TABLE I

ULTRAVIOLET ABSORPTION MAXIMA OF DEHYDRO-ANNULENES

Bisdehydro-[20]annulene				Tridehydro-[30]annulene			
Isoöctane		Benzene		Isoöctane		Benzene	
λmax, mμ	ε	λmax, mμ	ε	λmax, mμ	ε	λmax, mμ	ε
319	109,000	325	107,000	315	44,000	323	47,000
336	74,000	343	76,000	387[a]	112,000	..	....
				397	114,000	406	108 000

[a] Inflection.

Although the exact structure of the tridehydro-[30]annulene is not known with certainty, symmetry considerations suggest a formulation such as XIII, containing the three acetylenic bonds and three *cis*-ethylenic bonds each in a 1,11,21-relationship. It is to be noted that as in the rearrangement of the cyclic pentamer of 1,5-hexadiyne to pentadehydro-[30]annulene,[2] the rearrangement of XII to tridehydro-[30]annulene appears to have given rise to more than one isomer, as indicated by the variation in the ultraviolet spectra of suc-

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(20) It is to be noted, however, that whereas in the ultraviolet spectrum of tridehydro-[18]annulene and tetradehydro-[24]annulene the higher wave-length maximum of the main doublet is the more intense one, in the case of bisdehydro-[20]annulene it is the lower wave-length maximum which is the more intense.

(21) F. Sondheimer, R. Wolovsky and Y. Amiel, *J. Am. Chem. Soc.*, **84**, 274 (1962).

cessive chromatographic fractions (see Experimental section). Moreover, the tridehydro-[30]-annulene was not obtained as well-defined regular crystals like bisdehydro-[20]annulene and it is not impossible that even the crystalline substance consists of a mixture of isomers, a possibility which also applied to pentadehydro-[30]annulene.[2]

It is of interest to note how comparatively well the prototropic rearrangement of the cyclic dimer IX and trimer XII to the corresponding dehydroannulenes has proceeded, in contrast to the rather unsatisfactory results obtained when the cyclic dimer and trimer (IX and XII, replace non-conjugated acetylenic bonds by *trans*-ethylenic bonds) derived from *trans*-5-decene-1,9-diyne were subjected to an analogous rearrangement in order to obtain the annulenes directly.[17] These observations are in keeping with our findings in the acyclic series that the isomerization of linear 1,5-diynes to the conjugated polyen-ynes[5] with potassium *t*-butoxide proceeds with considerably great facility and in higher yield than the corresponding isomerization of linear 1,5-enynes to the conjugated polyenes.[22]

TABLE II

ULTRAVIOLET ABSORPTION MAXIMA OF ANNULENES

[20]Annulene				[30]Annulene			
From bisdehydro-[20]annulene (isoöctane)		From cycloeicosadiene-tetrayne (pentane)[17]		From tridehydro-[30]annulene (benzene)		From pentadehydro-[30]annulene (benzene)[21]	
λ_{max}, mμ	Optical density	λ_{max}, mμ	Optical density	λ_{max}, mμ	Optical density	λ_{max}, mμ	Optical density
267	0.81	268–272	1.13	329	0.29	331	0.22
284	.83	283	1.61	431	0.73	432	0.73
297	.81	297	0.87				
..	..	312	.69				
375	.20	373	.26				
396	.19	394	.24				

The above described bisdehydro-[20]annulene (*e.g.*, X) was partially hydrogenated in benzene solution over a Lindlar lead-poisoned palladium–calcium carbonate catalyst.[23] The reaction was terminated when 3 molar equivalents of hydrogen had been absorbed (no slowing down of gas absorption was observed), previous experiments in the C_{18}- and C_{24}-series having shown the advisability of allowing more than the theoretical amount of hydrogen to be taken up.[21] Chromatography on alumina then yielded first 25% of the desired [20]-annulene (*e.g.*, XI), followed by *ca.* 35% of unchanged bisdehydro-[20]annulene. There were no indications that any other substance with a characteristic ultraviolet spectrum had been formed.

[20]Annulene was obtained as a yellow oil which could not be induced to crystallize, neither directly nor after rechromatography. The ultraviolet spectrum is presented in Table II and Fig. 2. That all the five maxima belong to the same chromophore was shown by the fact that the spectra of successive chromatographic fractions containing this substance were essentially identical and remained unchanged on rechromatography. In keeping with the assigned structure, the infrared spectrum of [20]-annulene no longer showed an acetylene band in the 4.5–4.7 μ region,[12b] while full hydrogenation led to cycloeicosane. Further structural evidence is provided by the fact that the above-mentioned potassium *t*-butoxide rearrangement of the cyclic dimer of *trans*-5-decene-1,5-diyne, a reaction which also was expected to yield [20]annulene, had led to crude yellow oily chromatographic fractions with similar ultraviolet properties (see Table II).[17] It is not possible at present to state whether the [20]annulene from X possesses the 1,5,11,15-tetra-(*cis*)-ene structure XI, or a stereoisomeric one; it may also consist of a mixture of stereoisomers.

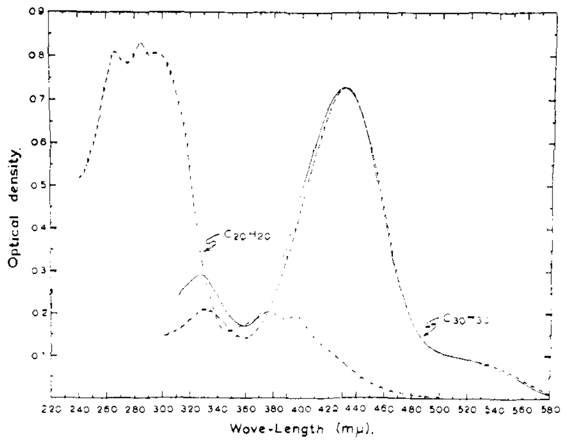

Fig. 2.—Ultraviolet absorption spectra of [20]annulene ($C_{20}H_{20}$) in isoöctane and [30]annulene ($C_{30}H_{30}$) in benzene (solid line, from tridehydro-[30]annulene; broken line, from pentadehydro-[30]annulene[21]).

Finally, the tridehydro-[30]annulene (*e.g.*, XIII) was subjected to partial hydrogenation in benzene solution over a Lindlar palladium catalyst.[23] Again, no slowing down of gas absorption was observed, and the reaction was interrupted when 4 molar equivalents of hydrogen had been taken up. Chromatography on alumina then led to a considerable amount of unchanged starting material, following by *ca.* 6% (determined spectroscopically) of [30]annulene (*e.g.*, XIV) contained in orange-red fractions which as noted before proved to be quite strongly adsorbed on alumina.[21]

Although the amount of [30]annulene formed was insufficient to permit of its isolation and direct comparison with the material obtained previously by partial hydrogenation of pentadehydro-[30]-annulene,[21] it is significant that the ultraviolet spectra of the [30]annulenes obtained by the two routes are very similar to each other (see Table II and Fig. 2).[24] Furthermore, no separation could be observed when a mixture of the two [30]annulenes was carefully chromatographed on alumina. These findings point to a [30]annulene structure for the partial hydrogenation product from XIII, and suggest that the [30]annulenes from the

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[22] F. Sondheimer, D. A. Ben-Efraim and R. Wolovsky, *J. Am. Chem. Soc.*, **83**, 1675 (1961).

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

[24] In Table II and Fig. 2 the optical density values of the main maxima of the [30]annulenes have arbitrarily been assumed to be identical. Actual density values could not be compared, since the spectrum of the [30]annulene described in this paper was measured only qualitatively.

two routes possess the identical steric configuration, presumably the symmetrical structure XIV in which hydrogen–hydrogen interaction is at a minimum in the planar molecule. However, the possibility cannot be excluded with certainty that the two [30]annulenes in fact differ in their stereochemistry (or represent stereoisomeric mixtures), and that such differences do not cause marked changes in the ultraviolet spectrum and in the strength of adsorption on alumina.

Of the four fully conjugated macrocyclic compounds described in this paper, bisdehydro-[20]-annulene (*e.g.*, X) and [20]annulene (*e.g.*, XI) were expected to be non-aromatic since they do not obey Hückel's rule [presence of $(4n + 2)$ π-electrons],[25] whereas tridehydro-[30]annulene (*e.g.*, XIII) and [30]annulene (*e.g.*, XIV) should be aromatic as these two substances obey Hückel's rule ($n = 7$)[26] and they can presumably take up a planar or nearly planar configuration. So far, no experimental data (*e.g.*, the n.m.r. spectra) bearing directly on this point have been obtained. None of the conjugated compounds showed any unusual stability, although both bisdehydro-[20]annulene and tridehydro-[30]annulene were considerably more stable than the corresponding annulenes; *e.g.*, both the dehydro compounds could be kept essentially unchanged without solvent for 24 hr., or in dilute benzene solution for 14 days (all experiments conducted at room temperature in air without protection from diffuse day-light), conditions under which the two annulenes suffered considerable decomposition.

Experimental[28]

***trans*-1,5,9-Decatriene (III).**—Allylmagnesium bromide (II) was prepared by the method given in ref. 11, a solution of 242 g. (2.0 moles) of allyl bromide in 170 cc. of ether being added dropwise during 7 hr. to a mixture of 118 g. (4.85 moles) of magnesium and 1400 cc. of ether, with stirring and continuous ice-cooling. The resulting Grignard reagent was filtered through glass wool into a second flask, and a solution of 107 g. (0.5 mole) of *trans*-1,4-dibromo-2-butene (I)[10] in 200 cc. of ether was added dropwise during 2 hr., again with stirring and ice-cooling. The mixture, which had separated into two layers, was allowed to reach room temperature and was then left overnight. A solution of 9 cc. of acetic acid in 36 cc. of water was added, followed by 300 cc. of water. The ether layer was separated, washed four times with a 10% sodium bicarbonate solution and three times with a saturated sodium chloride solution. The dried extract was evaporated and the residue was distilled rapidly under reduced pressure. The resulting liquid (52 g.), b.p. 60–72° (18 mm.), was then distilled through a 20-cm. Vigreux column. The first fraction (10.5 g.), b.p. 61–62° (18 mm.), n^{25}D 1.4389, which appears to be an alcohol (infrared bands at 2.77 and 2.91 μ) was not investigated further. The second fraction consisted of the required *trans*-1,5,9-decatriene (33.4 g., 49.1%), b.p. 69–70° (18 mm.), n^{25}D 1.4447; no high-intensity absorption in the ultraviolet; infrared bands (chloroform) at 6.09(s), 10.10(s) and 10.94(s) μ (monosubstituted ethylene)[12a] and 10.33(s) μ (*trans*-disubstituted ethylene).[12a]

Anal. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 87.82; H, 11.63.

1,2,5,6,9,10-Hexabromodecane (IV).—Bromine (57 g., 0.357 mole) was added during 25 minutes to a solution of 16 g. (0.118 mole) of *trans*-1,5,9-decatriene (III) in 150 cc. of pentane, with continuous stirring and ice-cooling. During the addition, a copious white precipitate separated; the supernatant liquid at the end was yellow, indicating the presence of excess bromine. The resulting hexabromide IV (52.2 g., 71.8%), obtained by filtering the mixture and washing the precipitate several times with cold pentane, formed colorless crystals, m.p. 111–112°. Crystallization of a sample from chloroform–ethanol led to the analytical specimen, m.p. 114–115°. The infrared spectrum (chloroform) showed the absence of double bonds (no bands at *ca.* 6.1 μ or in the 10–11 μ region).

Anal. Calcd. for $C_{10}H_{16}Br_6$: C, 19.51; H, 2.62; Br, 77.87. Found: C, 19.77; H, 2.58; Br, 78.05.

The filtrate obtained after removal of the 52.2 g. of IV was washed with sodium thiosulfate solution and water, and was then dried and evaporated. The resulting oil on being allowed to stand overnight in ether–pentane furnished another 3.1 g. (4.3%) of crystals, m.p. *ca.* 85–100°. The mother liquors (12.5 g., 17.3%) formed a yellow oil which could not be crystallized, but the infrared spectrum of which was very similar to that of the pure crystalline hexabromide.

In another experiment, a solution of 263 g. (1.646 moles) of bromine in 100 cc. of carbon tetrachloride was added during 1 hr. to a stirred and ice-cooled solution of 74.5 g. (0.548 mole) of III in 400 cc. of carbon tetrachloride. Collection of the resulting precipitate and washing with pentane yielded 194.5 g. (57.7%) of the crystalline hexabromide IV, m.p. 113–114°, while the filtrate produced 130 g. (38.5%) of a yellow oil which did not crystallize.

1,5,9-Decatriyne (V). (a) **From 1,2,5,6,9,10-Hexabromodecane (IV) (Preparative Method).**—A suspension of sodamide in *ca.* 3 l. of liquid ammonia was prepared from 101 g. (4.39 moles) of sodium, the transformation being catalyzed by means of 0.5 g. of ferric nitrate hexahydrate,[13] and the mixture being cooled to *ca.* −45° with a Dry Ice-acetone-bath. A solution of 226 g. (0.367 mole) of the crystalline hexabromide IV in 700 cc. of tetrahydrofuran and 300 cc. of ether was then added dropwise during 1 hr. with stirring and continued cooling. The cooled mixture was stirred for another 4 hr. and was then left overnight without cooling to allow most of the ammonia to evaporate. Ether and ice-water were added carefully to the residue, some insoluble polymeric material was removed by filtration, and the ether layer was washed successively with water, dilute hydrochloric acid, sodium bicarbonate solution and water. Evaporation of the dried extract, followed by rapid distillation of the residue, furnished 20.5 g. of a liquid, b.p. 62–68° (2 mm.), which was dissolved in *ca.* 30 cc. of pentane and cooled to −15°. Collection of the resulting crystals and washing with cold pentane yielded 9.51 g. (19.9%) of 1,5,9-decatriyne (V) as large colorless soft plates, m.p. 46° (unchanged on recrystallization from pentane), b.p. 61–63° (2 mm.); no high-intensity absorption in the ultraviolet; infrared bands (chloroform) at 3.03(s) and 4.70 (m) μ (monosubstituted acetylene).[12b,14] Chromatography of the mother liquors on alumina, followed by elution with pentane and crystallization as before, furnished another 2.39 g. of the triyne V, m.p. 44–45° (total yield, 24.9%).

Anal. Calcd. for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 91.82; H, 7.66.

(b) **From 1,4-Dibromo-2-butyne (VI) and Propargyl Bromide (VII).**—A Grignard reagent[16] was prepared from 8.6 g. (0.354 mole) of magnesium and 42.5 g. (0.357 mole)

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[25] E. Hückel, *Z. Physik*, **70**, 204 (1931); "Grundzüge der Theorie ungesättigter und aromatischer Verbindungen," Verlag Chemie, Berlin, 1938; D. P. Craig in "Non-benzenoid Aromatic Compounds," Ed. D. Ginsburg, Interscience Publishers, Inc., New York, N. Y., 1959, Chapter I.

[26] The assumption is made that the thirty-membered ring is not so large that the predictions of Longuet-Higgins and Salem[27] regarding bond-alternation in very large annulenes apply.

[27] H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* (*London*), **A251**, 172 (1959); **A257**, 445 (1960).

[28] Melting points were taken on a Fisher–Johns apparatus and are uncorrected. All chromatograms were carried out with Alcoa activated alumina, grade F-20 (Aluminum Co. of America, Pittsburgh, Pa.). Ultraviolet spectra were taken on a Cary model 14 recording spectrophotometer; unless mentioned otherwise, the ultraviolet spectra of chromatography fractions were determined against ether (dilutions also being made with ether). Infrared spectra were measured on a Baird double-beam recording spectrophotometer with sodium chloride optics. Full hydrogenations were carried out in dioxane over platinum, as described in parts VIII[3c] and XIX[17] of this series. Analyses were performed in our microanalytical laboratory under the direction of Mr. Erich Meier.

of propargyl bromide (VII) (dried and freshly distilled)[29] by covering the magnesium with *ca.* 30 cc. of ether, adding 0.2 g. of mercuric chloride and then *ca.* 3 cc. of the propargyl bromide, the mixture being stirred in nitrogen; when the vigorous reaction had started, the remaining propargyl bromide dissolved in 140 cc. of ether was added without cooling at such a rate as to maintain a steady reflux. The mixture was stirred for a further 30 minutes, and a solution of 15 g. (0.071 mole) of 1,4-dibromo-2-butyne (VI)[15] in 65 cc. of ether was then added all at once (no apparent reaction). Cuprous chloride (0.4 g.) was added in small portions, when an exothermic reaction took place, the mixture heated spontaneously to reflux for *ca.* 10 minutes and two layers separated. After being stirred for a further 2.5 hr. at room temperature and for 1 hr. under reflux, the mixture was cooled and decomposed by addition of ice and dilute hydrochloric acid. The aqueous layer was washed with ether and the combined organic extracts were washed with water, dried and evaporated. The residue (4.3 g.) in the infrared (chloroform) showed a strong allene band at 5.10 μ[12b,30] as well as terminal acetylene bands at 3.04(s) and 4.71(m) μ. This material was dissolved in a little pentane and chromatographed on a column of 400 g. of alumina.

The first fractions, eluted with pentane, consisted of allenic material as shown by the infrared spectra (bands at 5.10(s), 5.87(m) and 11.76(s) μ.[12b,30] The later fractions, eluted with pentane–ether (5:1), consisted of the triyne V (0.15 g., 1.6%), as evidenced by the infrared spectra which were virtually identical with that of a sample prepared by method (a). Low temperature crystallization from pentane yielded crystals, m.p. 43–45°, undepressed on admixture with the above-described substance.

Preparation of the Cyclic Dimer IX, Cyclic Trimer XII, Linear Dimer VIIIa and Linear Tetramer VIIIb from 1,5,9-Decatriyne (V).—The triyne V (7.6 g.) was added to a mixture of 114 g. of neutral cupric acetate monohydrate and 760 cc. of pyridine (commercial grade, previously distilled over sodium hydroxide). The mixture then was heated to 55° (internal temperature) and stirred vigorously at this temperature under a reflux condenser for 4 hr. The mixture was cooled, filtered, and the solid was washed well with benzene, the washings being kept separately. The filtrate was evaporated to a small volume under reduced pressure, the residue was combined with the benzene washings, and was then washed with dilute hydrochloric acid and water. The dried extract on evaporation to dryness under reduced pressure furnished 3.72 g. of a solid residue (only comparatively weak terminal acetylene band at 3.03 μ in the infrared), which was dissolved in a little benzene and chromatographed on a column of 600 g. of alumina.

Elution with pentane–ether (7:2) yielded fractions which on evaporation and crystallization from pentane led to 120 mg. (1.6%) of the linear dimer, **1,5,9,11,15,19-eicosahexayne (VIIIa)**, as colorless plates, m.p. 141–142°, raised by further crystallization from pentane to m.p. 143–144° (without decomposition); infrared bands (KBr) at 3.03(s) and 4.71(w) μ (terminal acetylene) as well as at 4.43(w) and 4.62(w) μ (α,γ-diyne).

Anal. Calcd. for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 92.91; H, 6.98.

Full hydrogenation of VIIIa, followed by crystallization from methanol, smoothly yielded *n*-eicosane, m.p. 36–37°, undepressed on admixture with a previously described sample (m.p. 36–37°).[3b]

Elution with pentane–ether (3:1) furnished fractions which on evaporation and crystallization from ether produced 465 mg. (6.2%) of the cyclic dimer, **1,3,7,11,13,17-cycloeicosahexayne (IX)**, as colorless prisms, m.p. 230–231° dec.[31]; $\lambda_{\max}^{\text{isooctane}}$ 226, 238 and 255 mμ[32]; infrared bands (KBr) at 4.42 (w) and 4.62(w) μ (α,γ-diyne), no terminal acetylene band at *ca.* 3.03 μ. The compound was reasonably stable and could be kept in the crystalline state for several weeks without appreciable decomposition.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.91; H, 6.24.

Full hydrogenation of IX and subsequent crystallization from methanol–ethyl acetate furnished cycloeicosane, m.p. 60–61°, undepressed on admixture with a previously described sample (m.p. 61–62°)[3c]; a considerable m.p. depression was observed on admixture with cyclotriacontane (m.p. 57–58°).[3c]

Elution with pentane–ether (2:1) followed by crystallization from ether yielded 390 mg. (5.2%) of the cyclic trimer **1,3,7,11,13,17,21,23,27-cyclotriacontanonayne (XII)** as colorless plates, m.p. 198–199° dec.[31]; $\lambda_{\max}^{\text{isooctane}}$ 226, 236 and 255 mμ[32]; infrared bands (KBr) at 4.43(w) and 4.62(w) μ (α,γ-diyne), no terminal acetylene band at *ca.* 3.03 μ. On standing in light and air, the compound gradually became yellow.

Anal. Calcd. for $C_{30}H_{24}$: C, 93.71; H, 6.29. Found: C, 93.68; H, 6.27.

Full hydrogenation of XII and crystallization from methanol–ethyl acetate produced cyclotriacontane, m.p. 56–57°, undepressed on admixture with an authentic sample (m.p. 57–58°).[3c] The m.p. was depressed on admixture with cycloeicosane (m.p. 61–62°)[3c] as well as with cyclotetracontane (m.p. 76–77°).[3c]

Elution with pentane–ether (1:1) followed by crystallization from ether furnished 145 mg. (1.9%) of the linear tetramer **1,5,9,11,15,19,21,25,29,31,35,39-tetracontadodecayne (VIIIb)** as colorless crystals, m.p. 192–194° dec.,[31] which showed a terminal acetylene band at 3.03(s) μ in the infrared (KBr). The substance was unstable and rapidly polymerized on being allowed to stand in air and light, becoming pink-red. Full hydrogenation and subsequent crystallization from ethyl acetate yielded *n*-tetracontane, m.p. 79–80°, undepressed on admixture with a previously prepared sample (m.p. 80–81°).[8b]

Bisdehydro-[20]annulene (X or an Isomer).—A saturated solution of potassium *t*-butoxide in *t*-butyl alcohol (150 cc.) was added to 265 mg. of the cyclic dimer IX dissolved in 150 cc. of benzene, and the solution was boiled gently under reflux for 15 minutes. The cooled solution was poured into ice-water and ether, and the organic layer was washed repeatedly with water. The red extract (sharp ultraviolet maximum at 320 mμ) was dried, evaporated to *ca.* 5 cc. under reduced pressure and chromatographed on a column of 150 g. of alumina. Firstly pentane–ether (19:1) eluted yellow fractions with ultraviolet maxima at *ca.* 305 mμ which were not investigated further. Elution with pentane–ether (9:1 to 17:3) gave light red-brown fractions all of which showed sharp ultraviolet maxima at 318–319 mμ due to bisdehydro-[20]annulene, the spectroscopic yield being 71 mg. (27%). Evaporation of these fractions and crystallization from pentane yielded 42 mg. (16%) of bisdehydro-[20]annulene (X or an isomer) in two crops as dark brown-violet plates (dark brown when finely divided), m.p. 176–177° dec.[31] The ultraviolet spectrum (Table I and Fig. 1) remained unchanged on recrystallization. The infrared spectrum (KBr) showed bands at 3.31(m), 4.64(w), 6.31(w), 6.54(m), 6.95(w), 7.10(w), 7.49(w), 7.67(m), 7.97(w), 8.25(w), 10.06(s), 10.47(m), 10.73(w), 11.32(w), 11.91(w), 13.11(m) and 13.65(s) μ. A benzene solution was red-brown when concentrated and light yellow-brown when dilute.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.03; H, 5.95.

Full hydrogenation of bisdehydro-[20]annulene followed by crystallization from methanol–ethyl acetate gave cycloeicosane, m.p. 59–60°, undepressed on admixture with an authentic sample (m.p. 61–62°).[3c]

Tridehydro-[30]annulene (XIII or an Isomer).—A solution containing 200 mg. of the cyclic trimer XII in 100 cc. of benzene and 100 cc. of a saturated solution of potassium *t*-butoxide in *t*-butyl alcohol was boiled gently under reflux for 20 minutes. The cooled solution was poured into ice-water and benzene, and the organic layer was washed well with water. The resulting dark red benzene solution showed ultraviolet maxima (against benzene) at 321 and 397 mμ due to tridehydro-[30]annulene.

The solution was evaporated under reduced pressure to *ca.* 5 cc. and chromatographed on a column of 200 g. of alumina. Ultraviolet examination of the fractions showed that the tridehydro-[30]annulene was eluted with pentane–ether (1:1 to 1:4), a shift in the spectra from double maxima at 312 and 385 mμ with shoulder at 396 mμ (beginning) to

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[29] A. Kirrmann, *Bull. soc. chim. France*, [4] **39**, 698 (1926).

[30] *Inter al.*, see J. H. Wotiz and D. E. Mancuso, *J. Org. Chem.*, **22**, 207 (1957).

[31] Sample placed on rapidly heated block just below this temperature. Only polymerization occurred when the melting point was determined in the usual way.

[32] No accurate intensity values were obtained in view of the low solubility of the substance in isoöctane.

double maxima at 319 and 398 mμ with shoulder at 386 mμ (end) occurring. This is probably indicative of isomers being present. These fractions on combination [spectroscopic yield of tridehydro-[30]annulene, 38 mg. (19%)], evaporation and crystallization from ether–pentane yielded 21 mg. (10.5%) of tridehydro-[30]annulene (XIII or an isomer) as a dark brown-violet crystalline powder which decomposed without melting on attempted melting point determination. The ultraviolet spectrum (Table I and Fig. 1) was unchanged on recrystallization from ether; $\lambda_{max}^{dioxane}$ 320 and 401 mμ (ϵ 51,000 and 113,000). The infrared spectrum (KBr) showed bands at 3.31(m), 4.64(w), 7.07(w), 7.75(m), 10.03(s), 10.32(m), 10.74(w), 11.88(w) and 13.28(m) μ. A benzene solution was dark red when concentrated and orange when dilute. No satisfactory elemental analysis could be obtained.

Anal. Calcd. for $C_{30}H_{24}$: C, 93.71; H, 6.29. Found: C, 88.91; H, 6.30.

Full hydrogenation of tridehydro-[30]annulene and subsequent crystallization from methanol–ethyl acetate yielded cyclotriacontane, m.p. 56–57°, undepressed on admixture with an authentic sample (m.p. 57–58°).[3c]

[20]Annulene (XI or an Isomer).—A solution of 31 mg. of bisdehydro-[20]annulene (*e.g.*, X) in 15 cc. of benzene was shaken in hydrogen over *ca.* 30 mg. of a Lindlar palladium catalyst[23] at room temperature and atmospheric pressure. In 15 minutes 3 molar equivalents of hydrogen had been absorbed and the reaction was stopped. The catalyst was filtered off and the filtrate, after concentration under reduced pressure to *ca.* 2 cc., was chromatographed on 50 g. of alumina; 25-cc. fractions were collected and the progress of the chromatogram was followed by determining the ultraviolet spectra of representative fractions.

Fractions 14–20 (light yellow solutions), eluted with pentane–ether (19:1), contained the [20]annulene; they all showed practically identical spectra, with maxima at *ca.* 267, 284, 297, 375 and 396 mμ, the first three being the most intense. Fractions 27–39 (light red-brown solutions), eluted with pentane–ether (9:1 to 4:1), contained unchanged starting material [11.4 mg. (37%), estimated spectroscopically], as shown by their ultraviolet spectra.

The above-mentioned fractions 14–20 on combination and evaporation yielded 7.8 mg. (25%) of [20]annulene as a yellow oil which could not be crystallized. The ultraviolet spectrum is given in Table II and Fig. 2. The infrared spectrum (chloroform) no longer showed the acetylene band at 4.64 μ present in the precursor. Rechromatography on 10 g. of alumina gave fractions with essentially identical ultraviolet properties.

Full hydrogenation of [20]annulene (material recovered from the rechromatography), followed by chromatography on alumina, elution with pentane, and crystallization from methanol–ethyl acetate, yielded cycloeicosane, m.p. 55–58°, undepressed on admixture with an authentic sample (m.p. 61–62°).[3c]

[30]Annulene (XIV or an Isomer).—A solution containing 12 mg. of tridehydro-[30]annulene (*e.g.*, XIII) in 10 cc. of benzene was shaken in hydrogen over *ca.* 20 mg. of a Lindlar palladium catalyst[23] at room temperature and atmospheric pressure. After *ca.* 2 hr. 4 molar equivalents of hydrogen had been taken up and the reaction was terminated. The catalyst was removed, the filtrate was evaporated almost to dryness under reduced pressure, and the residue was chromatographed on 30 g. of alumina. Elution with pentane–ether (1:1 to 1:3) yielded unchanged starting material, as evidenced by the ultraviolet spectra. [30]-Annulene was seen to move down the column as a more polar band, which was eluted with ether to ether–ethyl acetate (49:1) to give orange-colored fractions with maxima in the 412–414 mμ region [spectroscopic yield, 0.71 mg. (5.8%), based on ϵ = 140,000 of the main maximum of pure [30]annulene[21]]. The best representative fraction showed λ_{max}^{ether} 325 and 414 mμ (*E* 0.155 and 0.460); $\lambda_{max}^{dioxane}$ 328 and 427 mμ (*E* 0.585 and 1.595). The ultraviolet spectrum in benzene of this fraction is compared in Table II and Fig. 2 with that of the previously described [30]annulene.[21] On admixture with a sample of crystalline [30]annulene[21] and careful chromatography, no separation could be observed.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.]

Comparative Rates of Homolysis of *exo* and *endo* Bonds in Norbornane and Norbornene Systems

BY MICHAEL M. MARTIN AND DON C. DE JONGH

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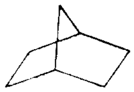
A kinetic study of the decompositions of *t*-butyl *exo*- and *endo*-bicyclo[2.2.1]heptane-2-percarboxylate and *exo*- and *endo*-bicyclo[2.2.1]hept-5-ene-2-percarboxylate has established that all four peresters decompose by a one-step, concerted loss of carbon dioxide. Comparison of the activation parameters for each pair of isomers indicates that homolysis of the *exo*-bond at C_2 is not assisted by the C_1–C_6 single bond or the C_5–C_6 double bond. Thus, non-classical radicals in these two systems can be ruled out in the rate-determining step.

Introduction

The products of free radical reactions involving the norbornane (I), norbornene (II), norbornadiene (III) and 2-methylenenorbornene (IV) systems can all be explained without postulating the intervention of non-classical free radicals. Norbornyl free radicals have been generated by hydrogen abstraction from norbornane derivatives,[1,2] by brominative decarboxylation of the silver salts of carboxylic acids in the dihydroaldrin series, a norbornane derivative,[3] by the decomposition of diacyl peroxides derived from dihydroaldrin carboxylic acids,[3] and by free radical addition reactions to norbornene derivatives.[4–6] In all cases, the products are best explained if they are derived from a radical having the classical structure V, rather than the non-classical structure VI. The free radical addition of *p*-thiocresol to norbornadiene leads to mixtures of the *exo*-5-norbornen-2-yl aryl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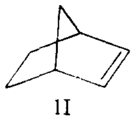
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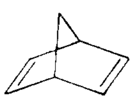
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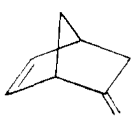
IV

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