cc. of acetic anhydride and 90 cc. of glacial acetic acid was boiled under reflux by means of an oil-bath for 1 hr., moisture being excluded. The cooled mixture was diluted with benzene, washed well with sodium bicarbonate solution and water, and was then dried and evaporated to dryness under reduced pressure. The amorphous residue (3.4 g.) showed $\lambda_{max}^{isooctane}$ 322, 335, 384 and 399 mμ, typical of VII. It was dissolved in a little benzene and roughly chromatographed on a column of 170 g. of alumina (Merck, acid-washed), in order to remove hydroxylic substances. The fractions eluted with pentane to pentane–ether (7:3) on evaporation yielded a total of 162 mg. of material, the ultraviolet spectrum of which indicated the presence of 16 mg. of VII (later fractions showed no maxima above 300 mμ on ultraviolet examination). This material was dissolved in *ca.* 1 cc. of benzene and re-chromatographed on a column of 100 g. of alumina (Aluminum Co. of America, grade F-20), which was washed with pentane and then with various mixtures of pentane–ether. The fractions eluted with pentane–ether (4:1), the only ones with ultraviolet maxima above 300 mμ, were combined, evaporated and crystallized from pentane. The resulting hexaene-triyne VII (11.2 mg., 0.12% over-all from Ia) formed brown plates, m.p. 190–192° (dec.; sample placed on block just before). It was identified with the previously described substance[1] by the complete identity of the ultraviolet spectrum (in isoöctane) as well as the infrared spectrum (in KBr). Furthermore, full hydrogenation (in dioxane over platinum), followed by crystallization from ethanol, smoothly yielded cycloöctadecane, m.p. 70–71°, undepressed on admixture with an authentic sample (m p. 71–72°).

(b) **With Phosphorus Oxychloride in Pyridine.**—Freshly distilled phosphorus oxychloride (10 drops) was added to a solution of 28.5 mg. of the crude lithium aluminum hydride product in 1.5 cc. of dry pyridine. The mixture was allowed to stand at room temperature for 20 hr., moisture being excluded, and was then poured on ice and extracted successively with pentane and ethyl acetate. The pentane extract was washed with dilute sulfuric acid, sodium bicarbonate solution and water, and was then dried and evaporated. The residue (1.4 mg.) showed ultraviolet maxima at 323, 335, 384 and 398 mμ (in isoöctane), typical of VII, with intensities indicating a purity of 6% (0.18% over-all yield from Ia). The ethyl acetate extract showed no well-defined ultraviolet maxima above 300 mμ.

Tridehydro-[18]annulene (VII) was also formed (as indicated by the ultraviolet spectrum of the product) when the dehydration with phosphorus oxychloride in pyridine was carried out at 60° for 15 minutes, but the yield appeared to be inferior.

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

Unsaturated Macrocyclic Compounds. XXIII.[1] The Synthesis of the Fully Conjugated Macrocyclic Polyenes Cycloöctadecanonaene ([18]Annulene),[2] Cyclotetracosadodecaene ([24]Annulene), and Cyclotriacontapentadecaene ([30]Annulene)

BY FRANZ SONDHEIMER, REUVEN WOLOVSKY AND YAACOV AMIEL

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Catalytic partial hydrogenation of tridehydro-[18]annulene (I) produces [18]annulene (cycloöctadecanonaene) (II), the first fully conjugated cyclopolyolefin after benzene for which aromatic character was predited. The physical and chemical properties of [18]annulene are described, and it is shown that this substance undergoes addition rather than substitution reactions. Evidence is presented, however, that this cyclopolyolefin in fact represents an aromatic system. Tetradehydro-[24]annulene (III) on similar partial hydrogenation yields [24]annulene (cyclotetracosadodecaene) (IV or V), an unstable substance which is theoretically non-aromatic; in addition a product is formed (apparently also produced by allowing [24]annulene to stand in solution), which is probably no longer monocyclic. The analogous partial hydrogenation of pentadehydro-[30]annulene (VI or an isomer) leads to the theoretically aromatic [30]annulene (VII or an isomer), a compound which proved to be quite unstable.

Introduction.—The synthesis and possible aromatic properties of macrocyclic hydrocarbons formally containing alternating single and double bonds (the annulenes)[2] have often been discussed.[3,4] Current theory predicts that such compounds should be aromatic provided their carbon skeleton can exist in a configuration which is planar or not far from planar, and they contain a closed shell of $(4n + 2)$ π-electrons ("Hückel's rule," met by annulenes made up formally of an odd number of double bonds).[5,6]

It has previously been pointed out by Mislow[7] that [10]annulene and [14]annulene,[8] the two members following benzene which comply with Hückel's rule, presumably cannot be planar in view of the steric interactions of the internal hydrogen atoms in the planar molecules as is evident from the scale drawings A and B.[9] These substances therefore do not meet one of the two criteria for aromaticity. It appeared to us from inspection of scale drawings that [18]annulene (C)[9] is the first member after benzene in which hydrogen–hydrogen interactions are not extreme and consequently in which the deviation of the carbon skeleton from coplanarity would not be great. [18]Annulene also complies with Hückel's rule ($n = 4$) and this substance was therefore the first cyclic polyene after benzene for which we anticipated aromatic character at the outset of our work (see also footnote 3c). This is in contrast to the conclusion of Mislow[7] who considered the interaction of the internal hydrogen atoms in [18]annulene still to

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[1] For Part XXII, see F. Sondheimer, Y. Amiel and Y. Gaoni, *J. Am. Chem. Soc.*, **84**, 270 (1962).

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

[3] For reviews, see (a) W. Baker and J. F. W. McOmie in "Progress in Organic Chemistry," Ed. J. W. Cook, Butterworths Scientific Publications, London, 1955, Vol. 3, Chapter 2; (b) W. Baker in "Perspectives in Organic Chemistry," Ed. Sir A. Todd, Interscience Publishers, Inc., New York, N. Y., 1956, p. 28; (c) W. Baker and J. F. W. McOmie in "Non-benzenoid Aromatic Compounds," Ed. D. Ginsburg, Interscience Publishers, Inc., New York, N. Y., 1959, Chapter 9; (d) M. E. Vol'pin, *Uspekhi Khim.*, **29**, 298 (1960) [English translation: *Russ. Chem. Revs.* (published by The Chem. Soc., London), 129 (1960)].

[4] For recent theoretical discussions of such systems, see O. E. Polansky, *Monatsh.*, **90**, 929 (1959); **91**, 898, 916 (1960).

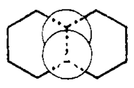
[5] E. Hückel, *Z. Physik*, **70**, 204 (1931).

[6] E. Hückel, "Grundzüge der Theorie ungesättigter und aromatischer Verbindungen," Verlag Chemie, Berlin, 1938.

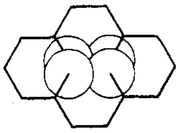
[7] K. Mislow, *J. Chem. Phys.*, **20**, 1489 (1952).

[8] F. Sondheimer and Y. Gaoni, *J. Am. Chem. Soc.*, **82**, 5765 (1960).

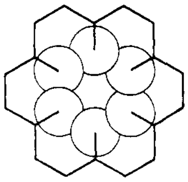
[9] The following dimensions have been used in drawing the diagrams A–D, following Mislow: carbon–carbon bond lengths (all equal), 1.40 Å.; carbon–hydrogen bond lengths, 1.10 Å.; hydrogen radii, 1.00 Å.; all angles 120 or 240°.



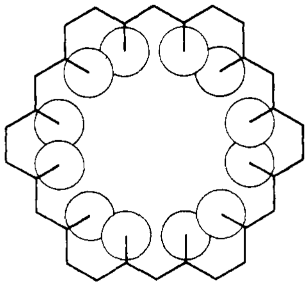
A



B



C

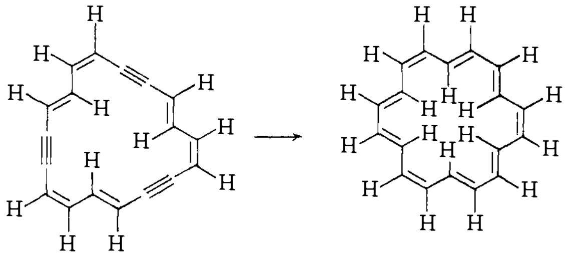


D

be large enough to prevent the compound from taking up a nearly planar configuration, a prediction supported by the recent calculations of Coulson and Golebiewski.[10] On this basis Mislow tentatively suggested[7] that [30]annulene (D) might be the first cyclic polyene after benzene to exhibit aromatic properties, since not only is Hückel's rule obeyed ($n = 7$), but also the deviation of the carbon skeleton from coplanarity should be even less than in [18]annulene as the degree of proximity which exists between *every* internal hydrogen atom in the C_{18}-compound exists only between *every alternate* internal hydrogen atom in the C_{30}-compounds.

Hitherto it has not been possible to test the above speculations experimentally since the only monocyclic conjugated polyolefins known were benzene and [8]annulene (cycloöctatetraene), despite many synthetic attempts to prepare other members. In the previous two papers of this series[1,2] we reported *inter al.* syntheses of the dehydro-annulenes I, III and VI (or isomers), containing 18, 24 and 30 carbon atoms in the ring. We now describe the conversion of these substances by partial hydrogenation to [18]annulene (II),[11a] [24]annulene (IV or V)[11b] and [30]annulene (VI or an isomer),[11c,12] respectively. Of these, the C_{18}- and C_{30}-compounds were expected to be aromatic (see above), while no aromatic properties were anticipated for the C_{24}-compound since this does not comply with Hückel's rule. The realization of the syntheses of these conjugated cyclic polyenes is of considerable importance since it makes possible the determination of their physical and chemical properties, and consequently enables us to test the validity of our theoretical ideas.

[18]Annulene (II).—Tridehydro-[18]annulene (I)[1,2] in benzene solution was hydrogenated at room temperature and atmospheric pressure over a Lindlar lead-poisoned palladium–calcium carbonate catalyst.[13] This catalyst in other cases had been shown to cause reduction of acetylenic to *cis*-ethylenic bonds, without affecting other ethylenic groupings (*inter al.*, footnote 13). Interruption of the reaction after 3 molar equivalents of hydrogen had been absorbed gave a solution, the ultraviolet spectrum of which exhibited a very sharp new band at 378 mμ (in benzene) besides bands indicative of the presence still of much starting material. Chromatography on alumina then yielded unchanged I, followed by a substance, subsequently shown to be [18]annulene (II), which crystallized as long brown-red needles (yellow-green in concentrated solution).



I II

The hydrogenation of I was performed a number of times under various conditions. It was found that the results obtained by use of a 10% palladium–charcoal catalyst were very similar to those obtained previously, and this became the preferred catalyst when it was observed that hydrogen was always taken up fairly rapidly by its use, in contrast to the Lindlar catalyst which at times caused the reaction to proceed very slowly or even to stop before the required amount of gas had been taken up. In order to elucidate the optimum amount of hydrogen to be absorbed, the hydrogenation of I in benzene over palladium–charcoal was allowed to proceed to completion,[14] aliquots being withdrawn at intervals and analyzed for [18]annulene and unchanged tridehydro-[18]annulene by ultraviolet examination. The result of this experiment, shown in Fig. 1, indicated that the optimum yield of [18]-annulene was 31–32% and was reached after 5–6 molar equivalents of hydrogen had been absorbed. Although the yield based on unrecovered starting material is higher when less than this amount of hydrogen is taken up, for preparative purposes it was found advantageous to let *ca.* 6 equivalents be absorbed, when comparatively little starting material remained[15]; the isolation of [18]annulene is

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[10] C. A. Coulson and A. Golebiewski, *Tetrahedron*, **11**, 125 (1960). These authors based their conclusion that [18]annulene is non-planar on the fact that the shortest hydrogen–hydrogen distances observed in aliphatic hydrocarbon crystals are *ca.* 2.50 Å., indicating a minimum value for the hydrogen van der Waals radius of *ca.* 1.25 Å

[11] For preliminary communications, see (a) F. Sondheimer and R. Wolovsky, *Tetrahedron Letters*, No. **3**, 3 (1959); (b) F. Sondheimer and R. Wolovsky, *J. Am. Chem. Soc.*, **81**, 4755 (1959); (c) F. Sondheimer, R. Wolovsky and Y. Gaoni, *ibid.*, **82**, 755 (1960).

[12] For an alternative synthesis of [30]annulene investigated by us, see F. Sondheimer, R. Wolovsky and D. A. Ben-Efraim, *ibid.*, **83**, 1686 (1961).

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

[14] No break in the rate of uptake of hydrogen was observed, although the rate progressively became slower until absorption stopped when *ca.* 12 molar equivalents had been absorbed. Very similar behavior was observed when the Lindlar catalyst was employed.

[15] Although the yields of [18]annulene were quite reproducible in repeated experiments, there was a certain variation in the amount of unchanged tridehydro-[18]annulene which remained. We have not been able to determine the exact factors responsible for this variation.

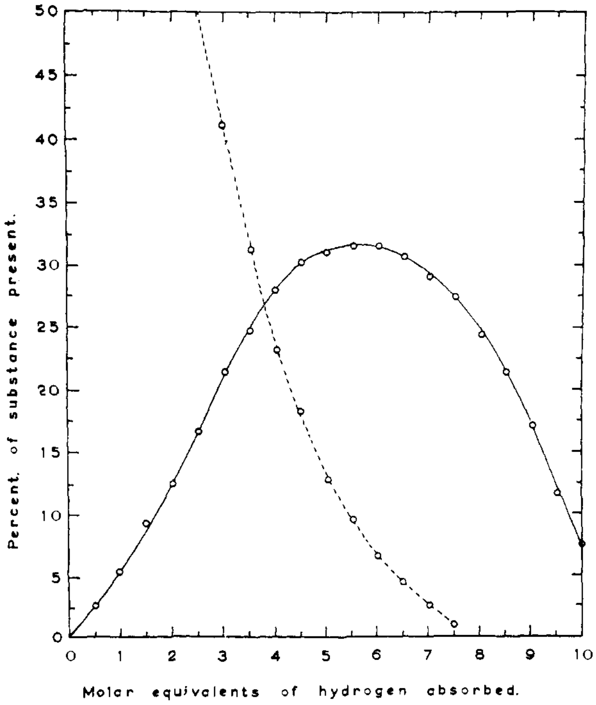

Fig. 1.—Amount of [18]annulene formed (solid line) and of unchanged starting material (broken line) during the catalytic hydrogenation of tridehydro-[18]annulene.

thereby facilitated since it is not easy to separate it efficiently from starting material by chromatography when both are present in comparable amounts in view of their similar polarities on alumina.

Under the optimum conditions, a yield of *ca.* 25% of pure crystalline [18]annulene could be realized. About 700 mg. of the cyclopolyolefin is therefore obtainable from 100 g. of 1,5-hexadiyne, as the yield in the conversion of this diyne to the crystalline precursor I is *ca.* 2.8%.[2]

The partial hydrogenation product derived from tridehydro[18]annulene was clearly an [18]annulene (cycloöctadecanonaene), since the elemental analysis indicated the formula $C_{18}H_{18}$, the infrared spectrum (Fig. 2)[16] no longer showed the acetylene band at 4.63 μ present in the precursor,[2] while hydrogenation in dioxane or acetic acid solution over platinum smoothly produced cycloöctadecane by absorption of almost exactly 9 molar equivalents of hydrogen.

Catalytic partial hydrogenation of acetylenes generally leads predominantly to the corresponding *cis*-ethylenes.[17] The [18]annulene would therefore be expected to possess 6 *cis* and 3 *trans* double bonds, a structure which is quite non-planar and in which the 9 double bonds could consequently not be effectively in conjugation. However, the ultraviolet spectrum of [18]annulene (Table I and Fig. 3)[18] indicates that all the double bonds in fact are in conjugation, as shown by the fact that the main maximum has been shifted by 35 mμ toward the visible and almost doubled in intensity (ε *ca.* 300,000!) compared with that of tridehydro-[18]annulene. This type of bathochromic shift and increase in intensity is usual when passing from a conjugated polyene-yne to the corresponding polyene.[19,20] In the preliminary communication[11a] we had therefore postulated the above-discussed structure II (diagram C, formally containing 3 *cis* and 6 *trans* double bonds) for the [18]annulene, derived from I by over-all *trans* addition of hydrogen. This formulation is not only in better accord with the ultraviolet spectral properties, but also accounts for the fact (which the non-planar structure with 6 *cis* double bonds does not) that the substance is *more* strongly adsorbed on alumina than its precursor I. The correctness of the structure II has now been established unequivocally by a 3-dimensional X-ray structure analysis which is being carried out at this Institute by Dr. J. Bregman and co-workers.[22]

TABLE I

ULTRAVIOLET ABSORPTION MAXIMA OF ANNULENES

[18]Annulene				[24]Annulene			
Isoöctane		Benzene		Isoöctane		Benzene	
λ_{max}, mμ	ε	λ_{max}, mμ	ε	λ_{max}, mμ	ε	λ_{max}. mμ	ε
269	7,600	..	.....	264	12,400	..	.....
278	8,100	..	.....	350	195,000	360	183,000
369	303,000	378	297,000	364	201,000	375	195,000
408	7,500	415	8,700	512	1,740	530	1,720
422	6,800	429	6,700	[30]Annulene			
448	21,800	456	28,400	Dioxane		Benzene	
				329	43,800	331	41,800
				428	144,000	432	140,000

While it has been noted previously that catalytic partial hydrogenation of acetylenes may give rise to small amounts of the *trans*-ethylenes in addition to the *cis* isomers,[23] the presently observed formation of *trans* double bonds in major amount in this type of reaction is unusual.[24] The observed stereochemical course of the hydrogenation of tridehydro-[18]annulene may well be a reflection of the two-step nature of the reaction.[25] Addition of one atom of hydrogen to a triple bond gives rise to a

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(16) A theoretical discussion of the infrared spectrum of this and of related conjugated macrocyclic compounds prepared by us will be published subsequently.

(17) *Inter al.*, K. N. Campbell and L. T. Eby, *J. Am. Chem. Soc.*, **63**, 216, 2683 (1941); K. N. Campbell and B. K. Campbell, *Chem. Revs.*, **31**, 77 (1942).

(18) For theoretical discussions of the ultraviolet spectrum, see (a) D. W. Davies, *Tetrahedron Letters*, No. **8**, 4 (1959); (b) M. Gouterman and G. Wagniere, *ibid.*, No. 11, 22 (1960); (c) H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* (*London*), **A257**, 445 (1960).

(19) *Inter al.*, compare the ultraviolet data of the linear polyeneynes described in Part XVIII of this Series (F. Sondheimer, D. A. Ben-Efraim and Y. Gaoni, *J. Am. Chem. Soc.*, **83**, 1682 (1961)) with those of the corresponding polyenes described in Part XVII (F. Sondheimer, D. A. Ben-Efraim and R. Wolovsky, *ibid.*, **83**, 1675 (1961)).

(20) It is also of interest that the position of the highest wave length maximum of [18]annulene at 456 mμ (in benzene) is almost identical with that of the linear model $CH_3(CH{=}CH)_9CH_3$ [454 mμ (in benzene) for the all-*trans* isomer[21a]; 456 mμ (in benzene) for an isomer presumably containing some *cis* double bonds[21b]].

(21) (a) F. Bohlmann and H. J. Mannhardt, *Ber.*, **89**, 1307 (1956); (b) F. Bohlmann, *ibid.*, **85**, 386 (1952).

(22) Private communication; see also J. Bregman and D. Rabinovich, *Acta Cryst.*, **13**, 1047 (1960).

(23) *Inter al.*, A. L. Henne and K. W. Greenlee, *J. Am. Chem. Soc.*, **65**, 2020 (1943); F. Sondheimer, *J. Chem. Soc.*, 877 (1950); D. E. Ames and R. E. Bowman, *ibid.*, 677 (1952).

(24) See A. Mondon, *Ann.*, **577**, 181 (1952), for the only other claim to the predominant formation of a *trans*-ethylene by the catalytic partial hydrogenation of an acetylene.

(25) *Inter al.*, J. Horiuchi and M. Polanyi, *Trans. Faraday Soc.*, **30**, 1164 (1934); R. K. Greenhalgh and M. Polanyi, *ibid.*, **35**, 520 (1939); R. A. Raphael, "Acetylenic Compounds in Organic Synthesis," Butterworths Scientific Publications, London, 1955, p. 24.

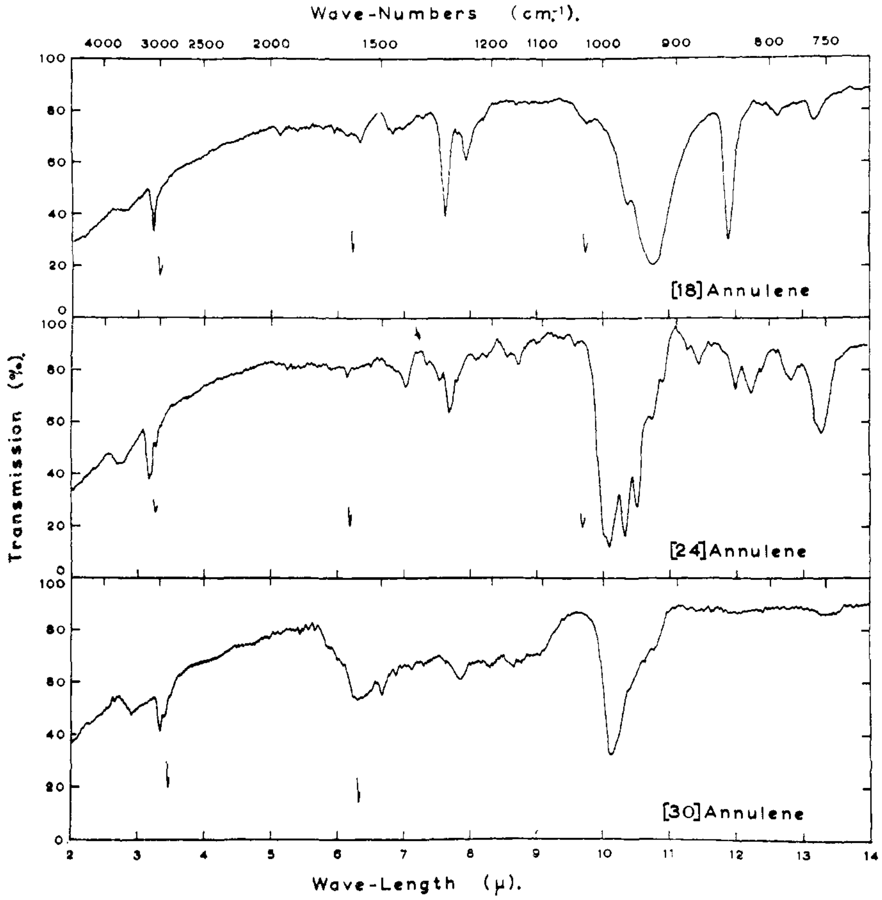

Fig. 2.—Infrared absorption spectra of annulenes, determined as KBr pellets with a Baird double-beam recording spectrophotometer (calibrated with polystyrene).

half-hydrogenated intermediate complex, which for steric reasons is forced to adopt an energetically more stable configuration to which the second hydrogen atom then adds in such wise as to produce the *trans*-ethylene. In this connection it is relevant to mention that in the partial hydrogenation of tridehydro-[18]annulene, the above-described [18]-annulene was the only new crystalline unsaturated material which could be isolated and the only new ultraviolet maxima were due to this substance, despite careful chromatographic analysis. It is however not impossible that a non-planar [18]annulene containing 6 *cis* double bonds was formed but was not detected, if such a substance is non-crystalline and shows no typical sharp high-intensity ultraviolet maxima as is the case with the non-planar [8]annulene.

The reduction of tridehydro-[18]annulene (I) was also attempted with chromous chloride in aqueous acetic acid,[26] with lithium aluminum hydride in boiling ether, as well as with lithium (6 molar equivalents) in liquid ammonia, since these reducing agents might have converted the acetylene bonds to *trans*-ethylenes and thereby resulted in an increased yield of [18]annulene. However, no detectable amount of this substance was obtained by use of any of these reagents, nor were other conditions (*e.g.*, zinc in ethanol or aqueous acetic acid)[26] more successful. A similar lack of success was encountered when attempts were made to prepare substituted [18]annulenes by the addition of various reagents (*e.g.*, diethylamine, hydrogen bromide or bromine) to tridehydro-[18]annulene.

In relation to the possible aromatic properties of [18]annulene (*vide infra*) it was of interest to investigate the stability of this substance and its behavior in typical electrophilic substitution reactions.

[18]Annulene, while being a reasonably stable compound, showed no very striking signs of stability. Thus, it could be sublimed on a small scale at *ca.* 130° under reduced pressure with comparatively little decomposition. It had no melting point, but underwent a color change at *ca.* 230° on being heated on a Kofler block, the needles becoming light yellow while retaining the crystal shape and remaining transparent; this change is non-reversible and appears to be due to the formation of polymeric material, since the recovered substance was completely insoluble in benzene.

The rate of decomposition in the solid state was found to depend markedly on the crystal size, large crystals prepared for X-ray measurements being much more stable than small ones either in daylight or in the dark. In benzene solution, the rate of decomposition was accelerated considerably by the presence of light as shown by the fact that a dilute solution was practically unchanged after 1 month

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[26] See B. S. Rabinovitch and F. S. Looney, *J. Am. Chem. Soc.*, **75**, 2652 (1953).

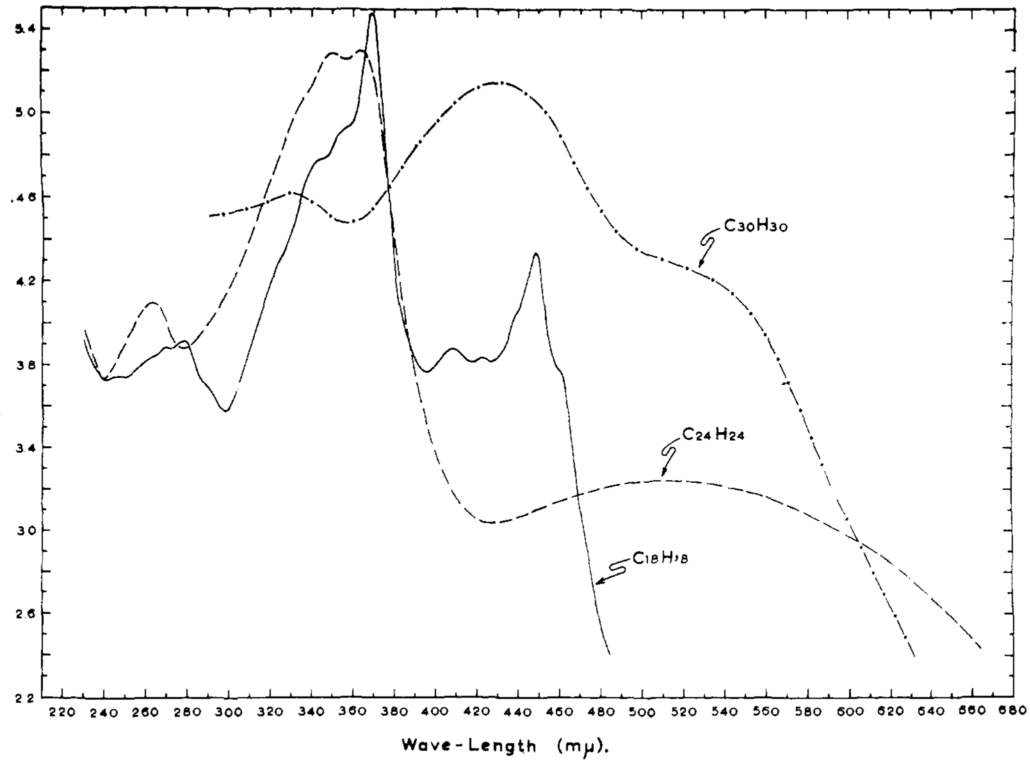

Fig. 3.—Ultraviolet absorption spectra of [18]annulene ($C_{18}H_{18}$) in isoöctane, [24]annulene ($C_{24}H_{24}$) in isoöctane, and [30]-annulene ($C_{30}H_{30}$) in benzene; determined with a Cary model 14 recording spectrophotometer.

in the dark, but *ca.* 65% had decomposed after this time when diffuse day-light was not excluded while over 99% had been destroyed when a more concentrated solution was allowed to stand for 2 hr. in direct strong sun-light.

[18]Annulene was subjected to attempted nitration, sulfonation, Friedel–Crafts acetylation and reaction with benzenediazonium chloride under conditions which had been employed successfully with non-benzenoid aromatic compounds such as azulene and cycl[3,2,2]azine (see Experimental section for details). In no case, however, could a product with a new ultraviolet spectrum be obtained, the reactions resulting either in recovery of unchanged starting material or else in its decomposition. On the other hand, [18]annulene exhibited the normal chemical properties of a conjugated polyene. Thus it underwent addition rather than substitution on treatment with an excess of bromine, as shown by the elemental composition of the ill-defined product which appeared to be made up by combination of *ca.* six molar equivalents of bromine with one of the cyclopolyene. Furthermore [18]annulene formed a Diels–Alder type of adduct with maleic anhydride in boiling benzene under conditions which left tridehydro-[18]annulene essentially unchanged, and it is readily hydrogenated catalytically as is evident from the above-described results (see also footnote 14). It is clear that [18]annulene in its reactions resembles an ordinary conjugated polyene rather than a typical benzenoid substance.

Finally, we wish to report some miscellaneous facts about [18]annulene. It has an unexpectedly low solubility in most organic solvents, a property which makes difficult the measurement of certain physical properties such as the nuclear magnetic resonance (n.m.r.) spectrum.[27] Unlike polycyclic aromatic hydrocarbons, it does not appear to form complexes with trinitrobenzene or with trinitrofluorenone. Moreover it is not extracted from organic solvents with aqueous silver nitrate (as is [8]annulene),[28] nor with concentrated phosphoric acid (as are azulenes)[29] in keeping with expectation.

[24]Annulene (IV or V).—Tetrahydro-[24]annulene (III)[2] was partially hydrogenated in benzene solution over a Lindlar palladium catalyst.[13] The reaction was terminated when 4 molar equivalents of hydrogen had been absorbed, although no slowing down of hydrogen uptake was observed. Ultraviolet examination of the resulting solution showed only the maxima at 333 and 350 mμ (in benzene) due to unchanged starting material, but an additional shoulder at 375 mμ had appeared. Chromatographic purification on alumina then yielded (in order of elution) lemon-yellow solutions with ultraviolet maxima at 305 and 314 mμ (in pentane) which are discussed further below, red solutions containing a considerable amount of unchanged tetradehydro-[24]annulene, and finally violet solutions containing the required [24]annulene. The last-mentioned substance crystallized as very dark-blue, almost black, needles (dark violet

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(27) The n.m.r. spectra of the annulenes described in this paper will be discussed in detail together with those of related conjugated monocyclic systems prepared by us in a separate publication.

(28) W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948); A. C. Cope and F. A. Hochstein, *J. Am. Chem. Soc.*, **72**, 2515 (1950).

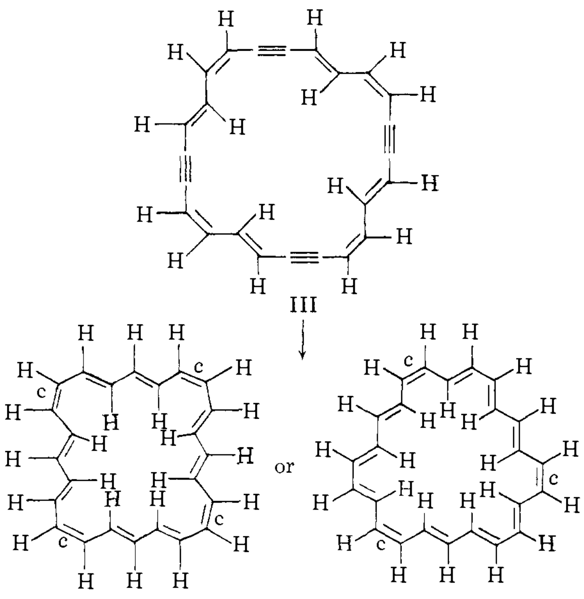
(29) *Inter al.*, A. S. Pfau and P. Plattner, *Helv. Chim. Acta*, **19**, 858 (1936).

in concentrated solution), which decomposed on attempted melting point determination.

The partial hydrogenation of tetradehydro-[24]-annulene was run a number of times, varying the amount of hydrogen taken up. Although the relationship between yield and hydrogen absorption was not studied as carefully as in the C_{18}-series in view of the fact that in no case was an ultraviolet maximum due to [24]annulene apparent in the total product, the best results appeared to be obtained when about 6 molar equivalents of hydrogen were allowed to be taken up. Preparative experiments were therefore run by absorption of 6 equivalents, resulting in a 15% yield of [24]annulene (determined spectroscopically; *ca.* 10% was isolated in crystalline form) besides the less polar yellow substance and unchanged starting material, as previously.

The dark-blue partial hydrogenation product must be a [24]annulene as it gave elemental analytical results in accord with the formula $C_{24}H_{24}$, the infrared spectrum (Fig. 2)[16] no longer showed the acetylene band at 4.62 μ present in the precursor,[2] and full hydrogenation in dioxane over platinum readily led to cyclotetracosane. The ultraviolet spectrum (Table I and Fig. 3)[30] indicates that as in the case of [18]annulene over-all *trans* addition of hydrogen appears to have taken place, since the main doublet is shifted by *ca.* 25 mμ toward the visible compared with tetradehydro-[24]annulene (though only the lower wave length maximum of the main doublet is increased in intensity, the other one being decreased slightly). Had the usual *cis* addition of hydrogen occurred, a completely non-planar [24]annulene containing 8 *cis* double bonds would have resulted which not only was expected to show maxima at lower wave lengths than the acetylenic precursor but also would very probably be *less* strongly adsorbed on alumina than this substance.

The [24]annulene presumably possesses either the 1,7,13,19-tetra-(*cis*)-ene structure IV or the 1,9,17-tri-(*cis*)-ene structure V (requiring the inversion of one *cis* double bond of the tetradehydro compound during the hydrogenation). The first of these is expected to show more deviation from coplanarity than [18]annulene (unless the bond angles are unusual) in view of the presence of 4 *cis* double bonds, whereas the second should show even less deviation since the degree of proximity which exists between *every* internal hydrogen atom in the C_{18}-structure II exists only between *every three* internal hydrogen atoms in the C_{24}-structure V. While the main ultraviolet maximum of [24]annulene falls at slightly lower wave length than that of [18]annulene, the position of the highest wave length maximum of the C_{24}-compound (at 512 mμ, in isoöctane)[31] is considerably higher than that of the highest wave length maximum of the C_{18}-compound (at 448 mμ, in isoöctane), and the former substance unlike the latter shows absorption beyond 650 mμ. Although the ultraviolet data do not allow a clear distinction between structures IV and V to be made, they tend to favor the more planar formulation V.[11b,18c] It should be noted that [24]-annulene, like [18]annulene, could not be converted to a more stable isomer, *e.g.*, by treatment with iodine in boiling benzene.



III

IV V

Other methods to determine whether the [24]-annulene possesses structure IV or V, involving the synthesis of a tridehydro-[24]annulene followed by partial hydrogenation to see if the same annulene as previously is formed,[32] as well as measurement of the n.m.r. spectrum,[27] were without success.

[24]Annulene does not obey Hückel's rule and therefore was not expected to exhibit aromatic properties. In view of the possible relationship between aromaticity and stability, the stability of this cyclic polyene was investigated. In practice [24]annulene proved to be quite a labile compound, the solid material suffering over 99% destruction on being allowed to stand at room temperature for 24 hours without protection from day-light; under the same conditions [18]annulene crystals of about equivalent size were essentially unchanged. Similarly [24]annulene in dilute benzene solution on standing for 12 days in the presence of day-light was nearly 80% destroyed, while less than 20% of [18]annulene had decomposed under the same conditions.

The violet chromatography fractions containing [24]annulene in pentane–ether solution on being allowed to stand for 7 weeks without exclusion of day-light had become lemon-yellow in color and ultraviolet maxima at 306 and 314 mμ (in pentane) had appeared. This transformation product, which could be crystallized though it was not obtained in pure form, appears to be the same as the material (which was also crystalline) contained in the above-described yellow solutions from the partial hydrogenation of tetradehydro-[24]annulene.

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(30) For theoretical discussions of the ultraviolet spectrum, see footnote 18c; H. Kuhn, *Chimia*, in press.

(31) It is of interest that the position of this maximum (at 530 mμ, in benzene) is fairly close to the value of *ca.* 515 mμ (in benzene) estimated for the highest wave-length maximum of the linear model $CH_3(CH{=}CH)_{12}CH_3$ from the curve relating the maxima of this type of polyene with the number of double bonds.[21a]

(32) F. Sondheimer and Y. Gaoni, to be published.

Identity was indicated by the similar ultraviolet spectra and the fact that a mixture could not be separated by chromatography on alumina. Full hydrogenation of the transformation product in dioxane over platinum led to a colorless crystalline substance, m.p. 242–245°, whereas cyclotetracosane shows m.p. 46–47°. It therefore seems very probable that the lemon-yellow material is no longer monocyclic, although its structure was not elucidated.

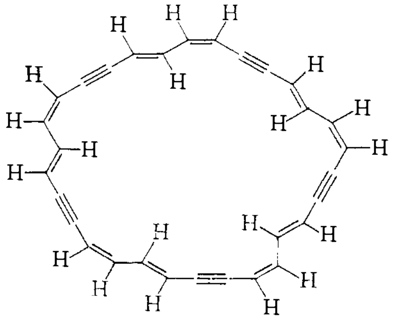
[30]Annulene (VII or an Isomer).—Pentadehydro-[30]annulene (VI or an isomer)[2] was partially hydrogenated in benzene solution over a Lindlar palladium catalyst.[13] The reaction was interrupted when 5 molar equivalents of hydrogen had been absorbed and the product was then chromatographed on alumina. Unchanged starting material was eluted first (with pentane–ether), followed by a much more strongly adsorbed red band which was not eluted until ether–ethyl acetate was employed. The new material, which proved to be the desired [30]annulene, was obtained as an unstable dark brown-red crystalline powder (dark red in concentrated solution), which decomposed on attempted melting point determination.

The yield of [30]annulene in this reaction was only *ca.* 6% (determined spectroscopically). In order to obtain sufficient material for complete identification, the partial hydrogenation was repeated with the mixture of uncrystallized pentadehydro-[30]annulene isomers as obtained from 1,5-hexadiyne by coupling, rearrangement and chromatography,[2] since this mixture is considerably more plentiful than the crystalline isomer. This preparative experiment gave similar results to those obtained previously, the spectroscopic yield of [30]annulene being *ca.* 4% and the yield of isolated crystalline substance *ca.* 2%.

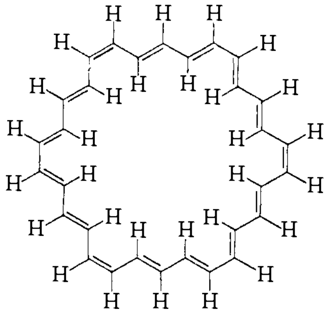
Although no satisfactory elemental analysis could be obtained, the results given by two different samples indicated a carbon:hydrogen ratio of 30:29.6 and 30:30.4, clearly pointing to a $C_{30}H_{30}$ formula. The infrared spectrum (Fig. 2)[16,33] no longer showed the acetylene band at 4.63 μ present in the pentadehydro compound,[2] whereas full hydrogenation in dioxane over platinum led to cyclotriacontane. It is on the basis of these facts that a [30]annulene structure was assigned to the partial hydrogenation product.

The ultraviolet spectrum of [30]annulene is given in Table I and Fig. 3.[18c,34] It is apparent that the position of the main maximum has been shifted by 32 mμ (in benzene) toward the visible compared with that of the pentadehydro compound,[2] although there is no significant change in intensity.[34] This fact, taken together with the observation that [30]annulene is considerably more strongly adsorbed on alumina than its precursor, provides evidence that over-all *trans* addition of hydrogen has taken place once again. Had *cis* addition occurred, a non-planar [30]annulene with at least 8 *cis* double bonds would have been formed which would not be expected to possess the observed properties.

It is not known with certainty at present whether the [30]annulene in fact possesses the above-mentioned symmetrical planar (or almost planar) 1,11,-21-tri-(*cis*)-ene structure VII (diagram D), or a stereoisomeric one. It is significant, however, that apparently the same [30]annulene is obtained by the partial hydrogenation of a tridehydro-[30]annulene,[35] whereas a different isomer would formally have been expected. This finding suggests that the stereochemistry of an annulene is not dependent on the number of *cis* and *trans* double bonds in the dehydro-annulene from which it is derived, but that the most stable configuration is generally formed. We therefore tentatively assign the structure VII to the [30]annulene since this is presumably the most favored configuration energetically, although no proof for this formulation is available at present.



VI



VII

[30]Annulene should represent an aromatic system if it indeed exists in the configuration VII. However, no experimental evidence bearing on this point has been obtained so far. It may be noted that [30]annulene proved to be a very unstable compound, suffering over 95% destruction on being allowed to stand at room temperature for 4 hours without protection from day-light, while solution in dioxane and chloroform also decomposed fairly rapidly (see Experimental section). This observed instability is consistent with our finding that an attempted alternate synthesis of [30]annulene, involving potassium *t*-butoxide rearrangement as the last step, did not lead to any clear-cut results.[12] The order of stability of the three annulenes described in this paper are [18]annulene > [24]annulene > [30]annulene.

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[33] The spectrophotometer was not operating well when this spectrum was determined and the curve is consequently rather unsatisfactory.

[34] It is probable that the intensity values are low, owing to some decomposition having occurred during the drying and weighing process.

[35] F. Sondheimer and Y. Gaoni, to be published; for a preliminary communication, see footnote 11c.

Discussion.—As mentioned in the Introduction, it was anticipated that [18]annulene and [30]annulene would exhibit aromatic properties. We hoped that this would manifest itself by these substances showing unusual stability and undergoing benzenoid-type of substitution reactions, since this might have led to much new chemistry. In the event, these cyclic polyenes did not at all resemble benzene in these respects and they cannot be considered "aromatic" in the classical sense.

There is, however, no theoretical justification for equating "aromaticity" with "stability" or "benzene-like chemical behavior" as has often been done, despite the fact that many aromatic substances do exhibit such behavior. A cyclic substance is aromatic if all the π-electrons are delocalized around the ring, *viz.*, if they form a closed electron shell. This is a property of the substance in its ground state, whereas chemical reactivity is dependent on the difference in free energy between that of the ground state and that of the transition state for the chemical change involved.[36] Valid criteria for aromaticity are such properties as a lower energy content than would be predicted by comparison with an appropriate acyclic analog, the ability to sustain an induced ring current of π-electrons, and the presence of carbon–carbon bonds which are intermediate in length between those usual for single and double bonds.

While a preliminary attempt to determine the energy content of [18]annulene through measuring the heat of hydrogenation[37] did not lead to a clear-cut result, the n.m.r. spectrum of this compound[27,38] clearly shows that it can indeed maintain an induced ring current. Moreover the above-mentioned 3-dimensional X-ray structure analysis,[22] though not yet complete, strongly suggests that the bonds do *not* alternate in length as they do, *e.g.*, in [8]annulene.[39] In the modern sense [18]annulene is therefore an aromatic system (in keeping with expectation), being in fact the first example of an aromatic macrocyclic polyolefin. We hope that further information regarding the aromaticity of the annulenes prepared in this paper will be forthcoming by measurement of such properties as the heat of combustion and the diamagnetic anisotropy, besides the previously mentioned properties.

The above-described annulenes contain a continuous molecular orbital, as indicated for [18]annulene in Fig. 4. Schematically this compound should be written as IIa rather than II (with separate single and double bonds), in view of the apparent lack of bond-alternation as revealed by the X-ray study. The latter in addition indicates [18]annulene to be a centrosymmetric molecule (a fact which by itself rules out bond-alternation), the carbon skeleton of which deviates from coplanarity by no more than 0.1 Å.[22] This last finding is of interest in view of the calculations of Coulson and Golebiewski[10] which led to the conclusion that the molecule must be far from planar.

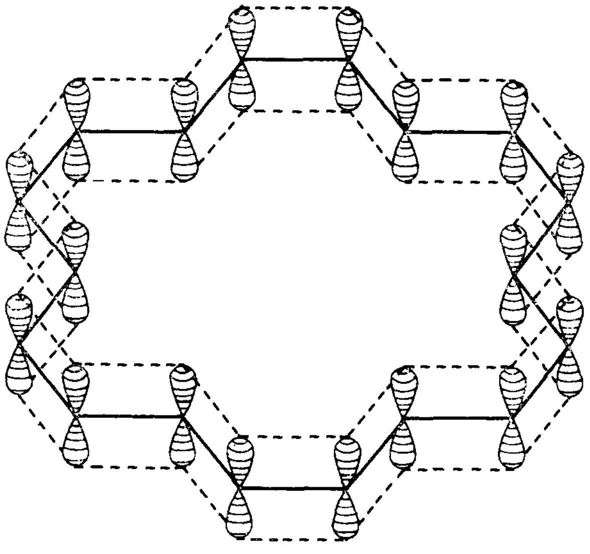
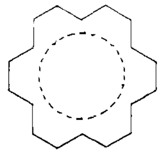
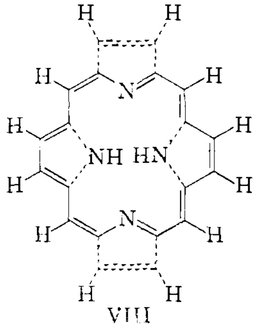


Fig. 4.—Molecular orbital diagram of [18]annulene.



IIa

Finally it is relevant to mention that porphine, the basic ring system of the leaf pigment chlorophyll and the blood pigment hemin, may be regarded as a derivative of 1,10-diaza-[18]annulene, as shown in formula VIII (*cf.*[3c]). Porphine and the derived porphyrins, as well as the phthalocyanines, are in fact the first known 18 π-electron systems related to [18]annulene. It is noteworthy that the n.m.r. spectra of porphyrins[40] are similar to those of [18]annulene as regards the "internal" and "external" protons.[27]



VIII

Experimental[41]

[18]Annulene (II) from Tridehydro-[18]annulene (I) (a) Investigation of the Hydrogenation.—A solution containing

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[36] For more extensive discussions regarding the nature of aromaticity, see D. P. Craig in "Non-benzenoid Aromatic Compounds," Ed. D. Ginsburg, Interscience Publishers, Inc., New York, N. Y., 1959, Chapter I; M. E. Vol'pin[3d]; W. von E. Doering and D. W. Wiley, *Tetrahedron*, **11**, 183 (1960); J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 859 (1961).

[37] Measured by Dr. R. B. Turner, Rice University, Houston, Tex.

[38] Measured by Dr. A. Bothner-By, Mellon Institute, Pittsburgh, Pa., and by Dr. L. M. Jackman, Imperial College of Science and Technology, London, Eng.

[39] This finding is contrary to the theoretical interpretation of the ultraviolet spectrum of [18]annulene, which is considered to favor a bond-alternating structure.[18b,c] A definite answer to this question must await the completion of the X-ray structure determination.

[40] E. D. Becker and R. B. Bradley, *J. Chem. Phys.*, **31**, 1413 (1959); J. Ellis, A. H. Jackson, G. W. Kenner and J. Lee, *Tetrahedron Letters*, No. **2**, 23 (1960).

[41] For general experimental details, see footnote 25 in Part XXI of this series.[2]

100 mg. of tridehydro-[18]annulene (I)[1,2] in 100 cc. of benzene was stirred in hydrogen over 25 mg. of a 10% palladium–charcoal catalyst (previously saturated with hydrogen) at 21° and 758 mm. in a flask fitted with a side-arm so that samples could be removed. Aliquots (0.5 cc. each) were withdrawn at intervals, diluted with benzene to known volume and the ultraviolet spectra were determined against benzene. The results are set out in Fig. 1,[14] the yield of [18]annulene being based on the intensity of the 378 mμ maximum and the amount of unchanged starting material on that of the 342 mμ maximum (corrections being made for the intensity of absorption at 342 mμ of pure [18]annulene and at 378 mμ of pure tridehydro-[18]annulene).

(b) **Preparative Experiment.**—The following is typical of the many different experiments carried out. A suspension of 75 mg. of a 10% palladium–charcoal catalyst in 40 cc. of thiophene-free benzene was stirred in hydrogen until equilibrium was reached. A solution of 1.04 g. of tridehydro-[18]annulene[2] in 60 cc. of benzene was then added and the mixture was stirred in hydrogen at 23° and 755 mm. until 669 cc. (6 molar equivalents) had been absorbed (*ca.* 1.5 hr.). Removal of the catalyst and ultraviolet examination of the resulting yellow-green solution against benzene showed that 32% of [18]annulene had been formed (based on the new 378 mμ maximum), while 5.5%[15] of unchanged starting material remained (based on the 342 mμ maximum, the same corrections as mentioned in experiment (a) being made). The solution was concentrated to *ca.* 10 cc. under reduced pressure and chromatographed on a column of 500 g. of alumina, which was washed with pentane and then with various proportions of pentane–ether. The progress of the chromatogram was followed by examining the ultraviolet spectra of representative fractions.

The fractions eluted with pentane–ether (17:3 to 4:1) consisted of unchanged starting material (main maxima at 322 and 334 mμ). The succeeding fractions, eluted with pentane–ether (4:1), contained both starting material and [18]annulene (maxima at 322, 334 and 369 mμ, the relative intensity of the last maximum steadily increasing in successive fractions). Finally pentane–ether (4:1 to 3:1) eluted fractions containing [18]annulene uncontaminated with the tridehydro compound (maximum at 369 mμ, but not at 322 or 334 mμ).

The fractions rich in [18]annulene were combined, concentrated to small volume and cooled. The resulting **[18]annulene (II)** (268 mg.; 25.1%, in two crops) formed small brick-red needles. Long regular brown-red lath-like needles having a metallic sheen (with identical ultraviolet properties) were obtained by recrystallization from chloroform or by storing the above-mentioned chromatography fractions containing [18]annulene without concentration at 0° for several days. For the behavior on attempted m.p. determination, see the Theoretical section. The ultraviolet data are given in Table I and Fig. 3. The infrared spectrum (Fig. 2) showed bands at 3.32(m), 6.33(w), 6.83(w), 7.63(s), 7.93(m), 9.72(w), 10.36(m), 10.72(s), 11.86(s), 12.60(w) and 13.16(w) μ. The substance could be sublimed on a small scale at 120–130° (0.05 mm.) with comparatively little decomposition. A benzene solution was yellow-green when concentrated and lemon-yellow when dilute. Of the various solvents investigated, the compound was most soluble in tetrahydrofuran (*ca.* 20 mg./cc.), less soluble in benzene, methylene chloride, chloroform, acetone, pyridine or dioxane (*ca.* 5–15 mg./cc. in each), and even less soluble in ether or isoöctane.

Anal. Calcd. for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.14; H, 7.69.

Microhydrogenation (carried out by Mr. E. Meier) of 1.910 mg. of [18]annulene in 1.35 cc. of glacial acetic acid over a trace of a pre-reduced platinum catalyst at 754 mm. and 24° resulted in the smooth absorption of 8.9 molar equivalents of hydrogen in *ca.* 45 minutes. Preparative hydrogenation of 12 mg. of [18]annulene in dioxane over platinum in the usual way,[41] followed by one crystallization from methanol–ethyl acetate, yielded 8.5 mg. of cycloöctadecane, m.p. 72–73°, undepressed on admixture with an authentic sample (m.p. 72–73°).

Stability Experiments with [18]Annulene.—Large crystals of [18]annulene (prepared for X-ray measurements) were found to be completely unchanged after being kept at room temperature without protection from day-light for 14 days, and less than 20% had decomposed after being stored at −15° in the dark for 6 months (as judged by dissolving the crushed substance in benzene and determining the intensity of the 378 mμ maximum). On the other hand, small crystals on being kept at room temperature had suffered over 50% decomposition after 7 days, either in day-light or in the dark; in the dark at −15°, 14% had decomposed after 7 days and over 50% after 6 months. A sample (small crystals) on being heated in a test-tube in air at 190° for 1.5 hr. had suffered 93% decomposition.

A solution of [18]annulene in benzene (0.35 mg./l.) on being allowed to stand in the dark at room temperature for 30 days was still 97% pure. The same solution on standing without protection from diffuse day-light showed the following rate of decomposition (determined by the optical density of the 378 mμ maximum)

Time, days	0	1	5	7	10	12	16	21	30
% of [18]annulene	100	98	94	90	87	83	75	58	35

More concentrated solutions were found to decompose more slowly. A benzene solution (16 mg./l.) on being illuminated for 2 hr. in a Pyrex flask in direct strong sun-light suffered over 99% decomposition.

Miscellaneous "Aromatic" Reactions Studied with [18]-Annulene. (a) **Nitration.**—A solution of 6 mg. of [18]-annulene in 1 cc. of acetic anhydride was added to 7.6 mg. of cupric nitrate trihydrate in 0.4 cc. of acetic anhydride at 0°.[42] After 20 minutes at 0°, the mixture was allowed to reach room temperature, aqueous sodium carbonate was added and the product was isolated with methylene chloride. The ultraviolet spectrum showed only the bands of unchanged starting material, and this was the only substance to be isolated after chromatography. In another experiment in which the reaction was allowed to proceed for 16 hr. at *ca.* 5°, decomposition had occurred as evidenced by the lack of any maxima in the ultraviolet.

(b) **Sulfonation.**—A solution of 5 mg. of [18]annulene in 2 cc. of dioxane was added at 0° to 5 cc. of dioxane containing 0.2 cc. of oleum. The mixture was shaken at 0° for 5 minutes and then poured into ice-water. Extraction with methylene chloride gave a product which showed only the maxima of unchanged starting material in the ultraviolet. Another experiment performed for 30 minutes at 0° resulted in complete decomposition as shown by the lack of any ultraviolet maxima.

(c) **Friedel–Crafts Reaction with Acetic Anhydride.** Treatment of a solution of [18]annulene in acetic anhydride at 0° with anhydrous aluminum chloride, stannic chloride or boron trifluoride etherate (in methylene chloride)[44] resulted solely in disappearance of the ultraviolet maxima. That these Lewis acids by themselves cause the destruction of [18]annulene was shown by the fact that the ultraviolet maxima disappeared when [18]annulene was treated with any of them in benzene, ether or methylene chloride at 0° in the absence of acetic anhydride. When the reaction was attempted by adding 0.01 cc. of 85% orthophosphoric acid to a solution containing 4.7 mg. of [18]annulene, 0.01 cc. of acetic anhydride and 0.2 cc. of methylene chloride,[45] followed by boiling under reflux for 30 minutes, over 80% of unchanged starting material remained (determined spectroscopically) and no new ultraviolet maxima had appeared.

(d) **Reaction with Benzenediazonium Chloride.**[46]—Benzenediazonium chloride was prepared from 100 mg. of aniline hydrochloride in the usual way. A solution of 7.2 mg. of [18]annulene and 145 mg. of sodium acetate in 5 cc. of ethanol was then added at *ca.* 10°. The color of the solution changed to brown and a solid brown mass separated. The mixture was allowed to stand at room temperature for 0.5 hr., water was added, and the product was extracted well with methylene chloride, followed by evaporation and chromatography on alumina. Although fractions with typical ultraviolet maxima were obtained, these were not derived from [18]annulene as evidenced by the fact that frac-

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[42] Azulene[43a] and cycl[3,2,2]azine[43b] have been nitrated successfully under comparable conditions.

[43] (a) A. G. Anderson, J. A. Nelson and J. J. Tazuma, *J. Am. Chem. Soc.*, **75**, 4980 (1953); (b) R. J. Windgassen, W. H. Saunders and V. Boekelheide, *ibid.*, **81**, 1459 (1959).

[44] Furans and thiophenes have been acylated under these conditions (M. W. Farrar and R. Levine, *ibid.*, **72**, 3695 (1950)).

[45] For the acylation of furans and thiophenes under these conditions, see H. D. Hartough and A. I. Kosak, *ibid.*, **69**, 3093 (1947).

[46] This experiment was based on the reaction of azulene with benzenediazonium chloride to give 1-azulenеazobenzene.[43a]

tions with identical ultraviolet properties resulted when the reaction was carried out in the absence of the cyclic polyene.

Reaction of [18]Annulene with Bromine.—A solution containing 200 mg. (1.25 mmoles) of bromine in 25 cc. of methylene chloride was added to 20 mg. (0.085 mmole) of [18]-annulene dissolved in 75 cc. of methylene chloride, and the solution was then allowed to stand in the dark at room temperature for 16 hr. when excess bromine was still present. The solvent was evaporated at room temperature under reduced pressure, the yellow solid residue was dissolved in a little ether and pentane was added. The resulting bromo compound was obtained as an almost colorless solid, m.p. *ca.* 190–240° dec., no maxima in the ultraviolet above 230 mμ. Attempted crystallization from methanol or chromatography on alumina or silica effected no marked purification. The elemental analysis pointed to the addition of between 5 and 6 moles of bromine, and clearly showed that addition rather than substitution had taken place.

Anal. Calcd. for $C_{18}H_{18}Br_{10}$: C, 20.92; H, 1.76; Br, 77.32. Calcd. for $C_{18}H_{18}Br_{12}$: C, 18.12; H, 1.52; Br, 80.36. Found: C, 19.30; H, 1.57; Br, 79.60 (C:H ratio = 18:17.45).

An experiment in which 8.5 mg. (0.053 mmole) of bromine in 8.5 cc. of methylene chloride was added to 6.2 mg. (0.0265 mmole) of [18]annulene in 2 cc. of methylene chloride, after 2 hr. at room temperature yielded unchanged starting material as sole material with a characteristic ultraviolet spectrum.

Reaction of [18]Annulene with Maleic Anhydride.—A solution containing 10 mg. (0.043 mmole) of [18]annulene and 75 mg. (0.77 mmole) of freshly sublimed maleic anhydride in 8 cc. of dry benzene was boiled under reflux for 4 hr., moisture being excluded. The resulting solution no longer showed the typical ultraviolet maxima of [18]annulene (a blank experiment in which maleic anhydride was omitted gave over 80% of unchanged starting material). The solvent was evaporated and excess anhydride was removed by heating the residue at *ca.* 70° (0.5 mm.). Crystallization of the solid residue from ethyl acetate–methanol yielded an almost colorless microcrystalline powder which did not melt below 300°; end absorption only in the ultraviolet; infrared bands at 5.43 and 5.63 μ (5-membered cyclic anhydride). The substance appears to be derived by addition of 4 moles of maleic anhydride.

Anal. Calcd. for $C_{34}H_{26}O_{12}$: C, 65.17; H, 4.18. Found: C, 64.75; H, 3.76.

Tridehydro-[18]annulene on treatment with maleic anhydride under identical conditions was recovered in *ca.* 90% yield (determined spectroscopically).

[24]Annulene (IV or V).—A solution of 500 mg. of tetradehydro-[24]annulene (III)[2] in 250 cc. of benzene was stirred in hydrogen over 1 g. of a Lindlar palladium catalyst[13] at 23° and 758 mm. After 240 cc. (6 molar equivalents) of hydrogen had been absorbed (in *ca.* 75 minutes), the reaction was interrupted and the catalyst was removed. Ultraviolet examination of the red filtrate against benzene showed the maxima at 333 and 350 mμ due to unchanged starting material, but a new shoulder at *ca.* 375 mμ was also apparent. The solution was concentrated under reduced pressure to *ca.* 15 cc. and then chromatographed on 1 kg. of alumina. Three separate colored bands (I, II and III) were observed to move down the column.

Band I, eluted with pentane–ether (17:3), yielded yellow solutions all of which showed ultraviolet maxima at *ca.* 305 and 314 mμ. Evaporation of these fractions produced 38 mg. of a "lemon-yellow" partially crystalline material, which appears to be also formed by decomposition of [24]-annulene in solution (see below).

Band II, eluted with pentane–ether (4:1), yielded orange-red solutions which proved to be unchanged starting material (maxima at 323 and 340 mμ). The recovery was *ca.* 25%, determined spectroscopically.

Band III (light violet on the column), eluted with pentane–ether (7:3 to 3:2), yielded violet solutions representatives of which all showed the main ultraviolet maxima at *ca.* 350 and 364 mμ typical of [24]annulene; the spectroscopic yield was 77 mg. (15.0%). Evaporation to small volume and cooling produced 51 mg. (9.9%) of **[24]annulene (IV or V)** in two crops as very dark-blue, almost black, needles which decomposed on attempted m.p. determination. The ultraviolet spectrum (Table I and Fig. 3) was unchanged on recrystallization from ether. The infrared spectrum (Fig. 2) showed bands at 3.31(m), 6.19(w), 7.06(w), 7.57-(w), 7.72(m), 8.75(w), 10.13(s), 10.36(s), 10.55(s), 10.77(m) 10.90(w), 11.47(w), 12.03(w), 12.25(w), 12.85(w) and 13.28-(m) μ. The compound could be sublimed (with partial decomposition) at 150–160° (0.0002 mm.). A benzene solution was dark violet when concentrated and red-violet when dilute. The substance was soluble in chloroform, tetrahydrofuran, dioxane and benzene, slightly soluble in isooctane and almost insoluble in pentane.

Anal. Calcd. for $C_{24}H_{24}$: C, 92.26; H, 7.74. Found: C, 92.14; H, 7.62.

Full hydrogenation in dioxane over platinum,[41] followed by one crystallization from methanol–ethyl acetate, furnished cyclotetracosane, m.p. 44–46°, undepressed on admixture with an authentic sample (m.p. 46–47°).

Stability Experiments with [24]Annulene.—A weighed sample of [24]annulene was allowed to stand at room temperature without protection from diffuse day-light for 24 hr. and was then crushed and triturated with warm benzene. A yellow-gray polymer remained insoluble and ultraviolet examination of the colorless solution showed that it contained less than 1% of starting material.

A solution of [24]annulene in benzene (0.52 mg./l.) on being allowed to stand at room temperature without protection from diffuse day-light showed the following rate of decomposition

Time, days	0	1	4	8	12
% of [24]annulene	100	91	66	37	21

More concentrated solutions were again found to decompose more slowly, as shown by the fact that a benzene solution (24 mg./l.) was essentially unchanged after 24 hr. standing as above; however, only 33% of [24]annulene remained when this solution was illuminated for 2 hr. with direct sun-light, whereas it was left essentially unchanged after illumination for 15 minutes with a Mazda ultraviolet lamp (with blue filter). In general, the effect of various solvents on the rate of decomposition of [24]annulene in solution was found to be: chloroform > ether > benzene > isoöctane.

A benzene solution of [24]annulene containing a trace of iodine after being boiled in the dark for 0.5 hr. showed an unchanged ultraviolet spectrum, except that the intensities of the maxima had dropped to *ca.* 75% of their original value due to some decomposition.

Transformation of [24]Annulene to the "Lemon-yellow" Compound.—Chromatography fractions containing by ultraviolet examination only [24]annulene, in pentane–ether (from the partial hydrogenation of tetradehydro-[24]annulene), were allowed to stand for 7 weeks on the bench without protection from diffuse day-light. By this time the violet solutions had become lemon-yellow and the ultraviolet spectra had become similar to those of the lemon-yellow fractions from the partial hydrogenation (appearance of maxima at 306 and 314 mμ). Evaporation to dryness yielded a partially crystalline yellow material, a sample of which was mixed with the lemon-yellow compound obtained before and chromatographed on alumina, whereby no separation could be achieved.

The yellow material from the decomposition of [24]annulene was hydrogenated in dioxane solution over a platinum catalyst until uptake of gas ceased. The catalyst and solvent were removed, and the residue, dissolved in a little ether, was filtered through a column of alumina. Pentane eluted a small amount of colorless oil, whereas ether eluted a substance crystallizing as needles, m.p. 242–245°, which was soluble in ether but almost insoluble in pentane.

[24]Annulene on being allowed to decompose in the solid state (see above) yielded no detectable amount of the "lemon-yellow" compound.

[30]Annulene (VII or an Isomer).—The chromatography fractions containing pentadehydro-[30]annulene (VI and/or isomers) (450 mg., determined spectroscopically), obtained from 1,5-hexadiyne by successive coupling, rearrangement and chromatography,[2] were evaporated, dissolved in 50 cc. of benzene and stirred in hydrogen over 500 mg. of a Lindlar palladium catalyst[13] at 24° and 752 mm. The reaction was interrupted when 146 cc. (5 molar equivalents) of hydrogen had been absorbed (in *ca.* 2 hr.). The catalyst was removed, the filtrate was concentrated to *ca.* 5 cc. under reduced pressure and the red solution was chromatographed on 800 g. of alumina.

The red fractions, eluted with pentane–ether (1:1 to 1:3), contained unchanged starting material as evidenced by the main ultraviolet maxima at 387–389 mμ. Subsequently red fractions were eluted with ether–ethyl acetate (49:1 to 19:1) which all showed a maximum in the 414–417 mμ region, due to [30]annulene (spectroscopic yield, 18 mg., 3.9%). These fractions were combined, evaporated and the residue was crystallized from ether. The resulting **[30]annulene (VII or isomer)** (9.5 mg., 2.1%) was obtained as a dark brown-red crystalline powder, which decomposed on attempted m.p. determination. The ultraviolet spectrum is given in Table I and Fig. 3.[34] The infrared spectrum (Fig. 2)[33] showed bands at 3.31(m), 6.61(w), 7.77(w), 10.00(s), 10.51(w) and 10.67(w) μ. A benzene solution was dark red in concentrated solution and orange-red in dilute solution.

Anal. Calcd. for $C_{30}H_{30}$: C, 92.26; H, 7.74. Found: C, 88.82, 88.52; H, 7.36, 7.52 (C:H ratio = 30:29.63, 30:30.38).

[30]Annulene with essentially identical physical properties was obtained (in *ca.* 6% spectroscopic yield) when the crystalline pentadehydro-[30]annulene isomer[2] was subjected to partial hydrogenation and subsequent chromatography as described above.

Full hydrogenation of [30]annulene in dioxane over platinum,[41] followed by crystallization from methanol, yielded cyclotriacontane, m.p. 56–57°, undepressed on admixture with an authentic sample (m.p. 57–58°).

Stability Experiments with [30]Annulene.—A weighed sample of [30]annulene was allowed to stand at room temperature in diffuse day-light for 4 hr. and then crushed and triturated with warm benzene. Ultraviolet examination showed that less than 5% of starting material remained.

A solution of [30]annulene in chloroform (*ca.* 0.68 mg./l.) which initially showed λ_{max} 429 mμ (*E* 0.250) on being allowed to stand without protection from diffuse day-light after 24 hr. showed λ_{max} 423 mμ (*E* 0.145) (at least 42% destruction) and after 48 hr. the maximum had disappeared (λ 423 mμ, *E* 0.088).[47] Similarly a solution of [30]annulene in dioxane (*ca.* 2 mg./l.) which initially showed λ_{max} 428 mμ (*E* 0.740) after 24 hr. in day-light exhibited λ_{max} 413 mμ (*E* 0.168), indicating at least 77% decomposition.

A benzene solution of [30]annulene (*ca.* 1.8 mg./l.) on being boiled with a trace of iodine was 45% destroyed after 5 minutes and completely destroyed after 1.5 hr.

Acknowledgments.—We are indebted to Dr. Y. Gaoni for valuable help in connection with the synthesis of [30]annulene, and to Dr. J. Bregman for very kindly allowing us to quote the preliminary results of the X-ray work on [18]annulene.

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[47] The instability in chloroform was first noticed when ether–chloroform was used to elute [30]annulene from the chromatography column, whereby extensive decomposition resulted.

[Contribution from the Chandler Laboratories, Columbia University, New York 27, N. Y.]

The Total Synthesis of *dl*-Dehydroabietic Acid[1]

By Gilbert Stork and John W. Schulenberg

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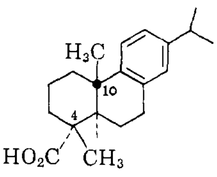
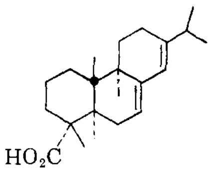
The total synthesis of *dl*-dehydroabietic acid is described.

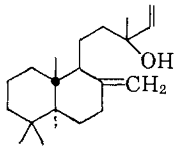
Dehydroabietic acid (I) has been shown by Harris[2] to constitute about 4% of the total acidic material obtained from the oleoresin of *Pinus palustris*. It is, however, because of its relationship to abietic acid (II), the major diterpene acid which is obtainable from rosin, that dehydroabietic acid derives its main interest. It is, in fact, from abietic acid that pure dehydroabietic acid was first obtained by Fieser and Campbell.[3] The extensive structural investigations which established the correct structure I of dehydroabietic acid have been reviewed in detail.[4] It is also known that the stereochemistry, both relative and absolute, is that shown in structure I. This last point was established by showing that dehydroabietic and abietic acids have the same relative and absolute stereochemistry of the A:B ring junction as manoöl (III)[5] which has in turn been correlated with lanosterol[6] (IV) and therefore with cholesterol.[7] The relative orientation of the methyl and the carboxyl groups at C_4 follows from the lack of optical activity of the tricarboxylic acid V obtained by nitric acid oxidation of abietic acid.[8]



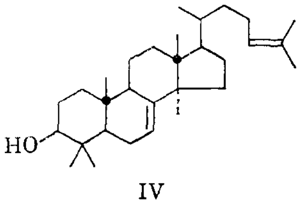
I



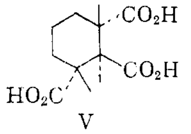
II



III



IV



V

We will describe in this paper the successful total synthesis of *dl*-dehydroabietic acid, but before we do this mention will be made of a few previous attempts.

Haworth and Barker[9] were the first to attempt the synthesis of dehydroabietic acid by a route

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[1] A preliminary report of this synthesis has been published, G. Stork and John W. Schulenberg, *J. Am. Chem. Soc.*, **78**, 250 (1956).

[2] G. C. Harris, *ibid.*, **70**, 3671 (1948).

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[4] L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," Third Edition, Reinhold Publishing Corp., New York, N. Y., 1949; J. L. Simonsen and D. H. R. Barton, "The Terpenes," Vol. III, Cambridge University Press, Cambridge, 1951.

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[9] R. D. Haworth and R. L. Barker, *J. Chem. Soc.*, 1299 (1939).