

Unsaturated Macrocyclic Compounds. XXXVII.¹ Cycloocatadecaheptaenetriyne and Cyclooctadecapentaene- tetrayne. Two New Dehydro[18]annulenes²

Reuven Wolovsky

Contribution from the Daniel Sieff Research Institute, The Weizmann Institute of Science, Rehovoth, Israel. Received March 20, 1965

*Oxidative coupling of 1,5-hexadiyne and subsequent rearrangement with potassium *t*-butoxide leads to the formation of two isomeric tridehydro[18]annulenes I and II as well as to a tetradecahydro[18]annulene III. Separation of the mixtures is achieved through reversible silver ion complex formation on chromatography columns or plates coated with silver nitrate.*

It has recently been shown³ that a tridehydro[18]-annulene is obtained when 1,5-hexadiyne is oxidatively coupled with cupric acetate in pyridine followed by rearrangement with potassium *t*-butoxide in *t*-butyl alcohol. We now wish to report that this reaction actually gives rise to two bond-sequence isomeric compounds (I and II). These isomeric tridehydro[18]annulenes could not be separated by crystallization or by the usual chromatographic procedures, but were successfully resolved through reversible silver ion complex formation on silver nitrate coated columns. In addition to compounds I and II, a tetradecahydro[18]annulene (III), the most highly unsaturated 18-membered ring system yet synthesized, is also formed.

In the oxidative coupling reaction of 1,5-hexadiyne to produce cyclic oligomers,^{3,4} 1,3,7,9,13,15-cyclooctadecaheptaenetriyne is formed from three C₆ units. This cyclic trimer when subjected to prototropic rearrangement into the fully conjugated system by treatment with a solution of potassium *t*-butoxide in *t*-butyl alcohol gives rise to a transformation of three acetylenic bonds and their adjacent methylenes into the corresponding conjugated α,γ -diene units. The facile⁵ mode of the rearrangement takes place because all the methylene hydrogens are activated (propargylic) and also because the resulting product, in this case, is stabilized through the formation of an aromatic system.⁶ Theoretically, in a planar unstrained conjugated ring, two⁷ different bond

sequence isomeric molecules can result upon the formation of a compound composed of three *cis-trans* double bond units separated by triple bonds. One, in which all the *cis-trans* double bond units are in a head-to-tail sequence, is exemplified by formula I in Figure 1; the other, formula II in Figure 1, is a molecule where the sequence of one pair of *cis-trans* double bonds has been reversed into a head-to-head relationship. One could expect two such molecules to differ only to a minor extent in their properties and, as a result, be difficult to separate by crystallization or chromatography.

The coordination of the silver ion with unsaturated compounds (olefinic,^{8a} cycloolefinic,^{8b} conjugated,^{8a} acetylenic,^{8c} and aromatic^{8d}) has been well established. The formation of the silver ion complex at room temperature is known to be rapid and reversible.^{8a} This kind of reversible silver complex formation was successfully applied⁹ to effect separation of closely related olefin mixtures by the vapor phase chromatographic method using a silver nitrate-glycol stationary phase. The countercurrent method,¹⁰ column chromatography,^{11a,b} and also thin layer chromatography^{11c-f} separations based on silver ion complex formation were used in the fatty acids and steroid fields. The chromatographic techniques were carried out on silver nitrate coated adsorbents and enabled separations at room temperature of relatively high boiling unsaturated compounds differing only with respect to the unsaturation function. It was anticipated that the last mentioned method would be suitable for separation of the isomeric dehydroannulenes, and this approach has

Indeed this was in accord with our observation that heating in solution of either isomer did not lead to the transformation into a recognizably different, more stable conformation. Other models of molecules in which two out of the three triple bonds present in the molecule were bonded in an α,γ sequence were excluded from consideration on the ground of the infrared spectrum. One would expect the appearance of two bands in the 4.5 μ region for an α,γ -diacetylene unit while only one band was actually observed for the two tridehydro isomers (cf. Figure 3). Other arrangements where the three triple bonds are unsymmetrically distributed in the molecule were discarded on the ground that such an arrangement would result in much more strain in the molecule.

(8) (a) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, **60**, 836 (1938); (b) J. G. Traynham and M. F. Schnert, *ibid.*, **78**, 4024 (1956); (c) W. S. Dorsey and H. J. Lucas, *ibid.*, **78**, 1665 (1956); (d) L. J. Andrews and R. M. Keefer, *ibid.*, **71**, 3644 (1949).

(9) (a) E. Gil-Av, J. Herling, and J. Shabtai, *J. Chromatog.*, **1**, 508 (1958); (b) J. Shabtai, J. Herling, and E. Gil-Av, *ibid.*, **2**, 406 (1959); (c) J. Herling, J. Shabtai, and E. Gil-Av, *ibid.*, **8**, 349 (1962); (d) M. A. Muhs and F. T. Weiss, *J. Am. Chem. Soc.*, **84**, 4697 (1962).

(10) (a) H. J. Dutton, C. R. Scholfield, and F. P. Jones, *Chem. Ind. (London)*, 1874 (1961); (b) B. de Vries, *ibid.*, 1049 (1962).

(11) (a) B. de Vries, *J. Am. Oil Chemists' Soc.*, **40**, 184 (1963); (b) C. F. Wurster, J. H. Copenhaver, and P. R. Schaffer, *ibid.*, **40**, 513 (1963); (c) C. B. Barrett, M. S. J. Dallas, and F. B. Padley, *Chem. Ind. (London)*, 1050 (1962); (d) L. J. Moris, *ibid.*, 1238 (1962); (e) C. B. Barrett, M. S. J. Dallas, and F. B. Padley, *J. Am. Oil Chemists' Soc.*, **40**, 580 (1963); (f) H. K. Mangold, *ibid.*, **38**, 708 (1961).

(1) Part XXXVI: R. Wolovsky and F. Sondheimer, in press.

(2) Presented first before the Israel Chemical Society, Jerusalem, Dec. 1964; cf. R. Wolovsky, *Israel J. Chem.*, **2**, 300 (1964).

(3) (a) F. Sondheimer and R. Wolovsky, *J. Am. Chem. Soc.*, **81**, 1771 (1959); (b) F. Sondheimer and R. Wolovsky, *ibid.*, **84**, 260 (1962); (c) for other pertinent references, see F. Sondheimer, *Pure Appl. Chem.*, **7**, 363 (1963).

(4) F. Sondheimer, Y. Amiel, and R. Wolovsky, *J. Am. Chem. Soc.*, **79**, 4247 (1957).

(5) (a) F. Sondheimer, D. A. Ben-Efraim, and R. Wolovsky, *ibid.*, **83**, 1675 (1961); (b) F. Sondheimer, D. A. Ben-Efraim, and Y. Gaoni, *ibid.*, **83**, 1682 (1961); (c) F. Sondheimer, R. Wolovsky, and D. A. Ben-Efraim, *ibid.*, **83**, 1686 (1961).

(6) L. M. Jackman, F. Sondheimer, Y. Amiel, D. A. Ben-Efraim, Y. Gaoni, R. Wolovsky, and A. A. Bothner-By, *ibid.*, **84**, 4307 (1962).

(7) Models can be constructed of various planar conformational isomers differing in the *s-cis* and *s-trans* combinations. Such possibilities were excluded from consideration in this case because the energy barrier for this interconversion in solution would be expected to be low; thus even at room temperature the most stable conformer should be formed.

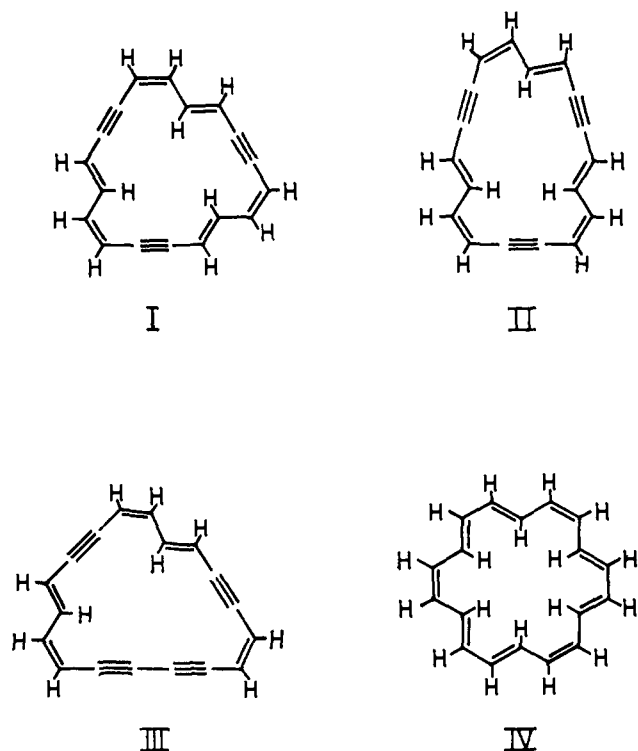


Figure 1.

been found to be realizable in practice.¹² Oxidative coupling of 1,5-hexadiyne¹³ with cupric acetate in pyridine was carried out as described previously^{3b}; the ratio of 1 part of diyne:100 parts of pyridine was maintained as in analogous preparations. The total product thus obtained was subjected to prototropic rearrangement with potassium *t*-butoxide in *t*-butyl alcohol-benzene solution for 30 min. at 100°. The mixture was subsequently subjected to chromatography over alumina to separate out the fractions rich in the C₁₈ products as before.^{3b} The separation on the alumina turned out to be less efficient than that achieved previously (see Experimental). The dehydro[18]annulene fractions appeared to be contaminated, in addition to small amounts of the C₂₄ compound and other impurities, also with the triphenylene and a yellow substance V showing λ_{max} 280 m μ . The latter, an unstable yellow solid, is most probably a rearranged linear C₁₈ compound derived from a linear trimer during the rearrangement process. Compound V did not produce cyclooctadecane upon full hydrogenation and was not further investigated. In order to remove triphenylene completely from the product mixture, chromatography over silicic acid was found most effective. The yellow substance V, however, did not separate on this column and had to be removed through an additional chromatography over Florisil. The dehydro[18]annulene now free from the accompanying impurities exhibited all the physical properties as described previously^{3b} for pure tridehydro[18]annulene. Thus the ultraviolet and infrared spectra were essentially unchanged upon recrystallization of the compounds from pentane-ether and they

(12) The formation of an isolable crystalline π -complex of tridehydro[18]annulene with an organic π -acid as, e.g., 1,3,5-trinitrobenzene, will be discussed separately: R. Wolovsky and F. Sondheimer, forthcoming publication.

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

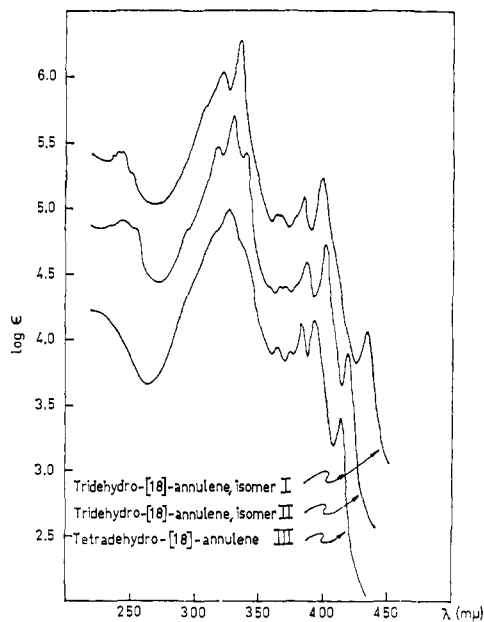


Figure 2. Ultraviolet absorption spectra of tridehydro[18]annulene isomer I, tridehydro[18]annulene isomer II, and tetrahydro[18]annulene (III) determined with a Cary Model 14 recording spectrophotometer in 2,2,4-trimethylpentane. The log ϵ value of I has been displaced (increased) by 1.0 unit and that of II has been displaced (increased) by 0.5 unit.

formed only one oval spot on a thin layer chromatograph (t.l.c.) plate (Kieselgel G), developed from pentane-ether (90:10). However, t.l.c. examination on a silver nitrate coated plate, developed with pentane-benzene (95:5), revealed three distinct spots. A preparative-scale elution chromatography over a 20% silver nitrate coated alumina column developed with pentane-benzene mixtures was carried out on the solution of the dehydro[18]annulene. Under these conditions, ready separation was achieved giving three distinct bands, out of which pure, crystalline compounds could be obtained.

The first band to be eluted yielded a very small amount (*ca.* 0.15% yield based on 1,5-hexadiyne) of brick-red crystals of tetrahydro[18]annulene (III). This structure is assigned on the following grounds. Elemental analysis of III proved it to have a C₁₈H₁₀ composition, while the ultraviolet spectrum, shown in Table I and Figure 2, indicated the presence of a highly conjugated system resembling that of a tridehydro[18]annulene.^{3b} In the infrared (see Figure 3), compound III showed two weak bands at 4.60 and 4.73 μ , indicating an α,γ -diacetylene, and also strong bands at 10.35 and 10.80 μ , due to conjugated *cis-trans* diene groupings. The absence of infrared bands in the 5.1- μ region excluded the presence of allenic functions. Platinum-catalyzed, full hydrogenation of III to cyclooctadecane proved that the substance retained the monocyclic C₁₈ skeleton during the rearrangement reaction; moreover, partial hydrogenation in benzene with a palladium on charcoal catalyst to produce [18]annulene¹⁴ confirmed the dehydroannulene nature. Finally the nuclear magnetic resonance (n.m.r.) spectrum of III (see Figure

(14) (a) F. Sondheimer and R. Wolovsky, *Tetrahedron Letters*, No. 3, 3 (1959); (b) F. Sondheimer, R. Wolovsky, and Y. Amiel, *J. Am. Chem. Soc.*, 84, 274 (1962).

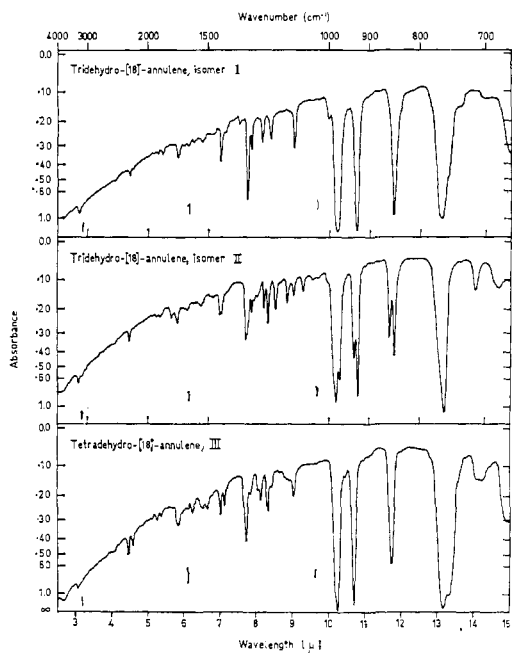


Figure 3. Infrared absorption spectra of tridehydro[18]annulene isomer I, tridehydro[18]annulene isomer II, and tetradehydro[18]annulene determined as KBr pellets with a Perkin-Elmer Infracord recording spectrophotometer and calibrated with polystyrene.

Table I. Ultraviolet Absorption Maxima of Dehydro[18]annulenes

I		II		III	
$\lambda_{\max}, m\mu (\epsilon)$		$\lambda_{\max}, m\mu (\epsilon)$		$\lambda_{\max}, m\mu (\epsilon)$	
2,2,4-Trimethylpentane					
233	(27,600)	234	(30,800)	228	(16,200)
237	(33,300)	244	(26,300)	297	(25,000)
244	(34,200)	253	(22,800)	316	(66,200)
252	(24,100)	295	(22,500)	327	(99,000)
295	(22,100)	310	(58,300)	338	(54,000)
313	(60,600)	318	(93,000)	354	(11,350)
322	(111,500)	331	(166,000)	363	(8,800)
335	(190,000)	340	(90,500)	374	(8,100)
364	(9,200)	358	(8,100)	383	(12,550)
368	(8,920)	367	(8,050)	395	(14,500)
378	(8,920)	370	(8,200)	414	(2,550)
385	(12,700)	380	(8,600)		
395 (sh)	(11,200)	387	(12,600)		
399	(16,900)	402	(16,800)		
433	(1,190)	420	(2,860)		
Benzene					
317	(80,000)	326	(89,800)	324 (sh)	(63,000)
328	(110,000)	338	(145,200)	334	(96,500)
343	(180,000)	347 (sh)	(94,700)	367	(9,000)
390	(12,600)	374	(8,950)	378	(8,050)
406	(16,500)	392	(11,600)	387	(11,800)
436	(1,050)	407	(16,000)	399	(14,050)
441	(1,150)			418	(2,420)

4) is in accord with the proposed structure. It consists of two multiplets; the one at τ 7.4–8.1 is assigned to the inner (shielded) protons and the second at 1.8–3.5 is assigned to the outer (deshielded) protons. The integrated areas were found to possess the ratio 1:4 as required by structure III. The n.m.r. spectrum thus confirms the compound to possess a tetradehydro[18]annulene structure. We consider the tetradehydro[18]annulene most likely to possess structure III, formally derived from I by substitution of a *trans* double bond by

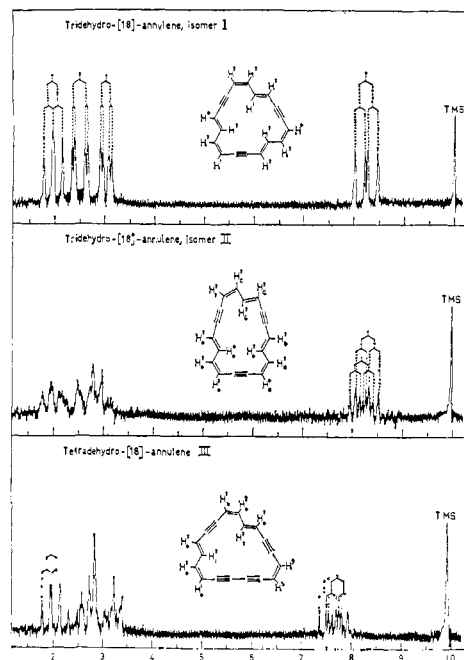
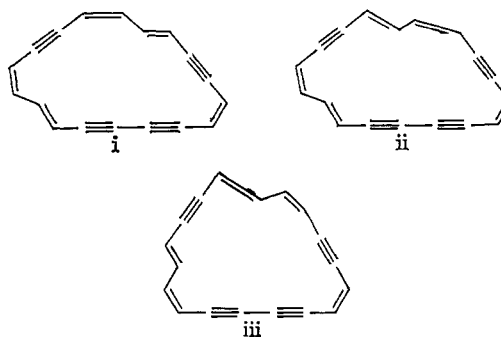


Figure 4. N.m.r. spectra of tridehydro[18]annulene isomer I, tridehydro[18]annulene isomer II, and tetradehydro[18]annulene. The spectra were taken on a Varian A-60 spectrometer in carbon tetrachloride at 60°. TMS was used as an internal reference.

an acetylene.¹⁵ In the high-field region (see Figure 4), two quartets with chemical shifts centered at τ 7.66 and 7.80 units are observed; these are due to the slightly different two H^a and H^b inner protons. Splittings due to the adjacent H^4 and H^2 protons gave coupling constants with values of $J_{H^a-H^4} = 15$ c.p.s. and $J_{H^b-H^2} = 12$ c.p.s., respectively. The coupling constants are in good agreement with the similar coupling constant values obtained for the two isomeric tridehydro[18]annulenes I and II (see further and also ref. 6). In the low-field region (τ 1.8–3.5), although no complete interpretation can be given to all peaks, partial assignment is possible. The multiplet in the τ 3.0–3.5 region, equivalent in area to two protons, is due to the (slightly different) two H^1 protons. Coupling constants of $J_{H^1-H^2} = 10$ c.p.s. due to the splittings of the adjacent H^2 protons can be observed though these are blurred out in part because of the small propargylic splittings due to H^4 and perhaps also to the neighboring H^5 protons. Two H^4 plus two H^5 protons appear as the multiplet at the τ 2.2–3.0-region. The remaining two H^2 protons appear as a triplet (degenerate quartet) with

(15) However, the possibility that the tetradehydro[18]annulene is formally derived from structure II leading, e.g., to i, ii, or iii cannot be excluded on the basis of the n.m.r. spectrum.



a chemical shift centered at τ 2.03. The appropriate coupling constants $J_{H^2-H^3} = 12$ c.p.s. and $J_{H^2-H^4} = 10$ c.p.s. due to the splittings by the adjacent H^3 and H^4 protons are observed.

The formation in very small yield of a tetrahydro[18]annulene in this reaction can be explained as resulting from dehydrogenation (oxidation) by potassium *t*-butoxide and oxygen from the air.¹⁶ A similar dehydrogenation has been observed in the [14]annulene^{16c} series.

The next two bands to be eluted from the chromatography column gave solutions out of which the two isomeric tridehydro[18]annulenes could be crystallized. Both isomer I and isomer II furnished upon crystallization from pentane-ether light brown, rectangular plates indistinguishable by their outward appearance.

The first of the two eluted compounds, tridehydro[18]annulene isomer I, was the major component (*ca.* 75% of the C_{18} dehydro compounds). It exhibited properties differing only slightly from those published^{3,6} for tridehydro[18]annulene, indicating that the latter was predominantly isomer I with only small amounts of the other dehydro[18]annulene. The ultraviolet spectrum of pure isomer I is given in Table I and Figure 2; for the infrared spectrum of the above see Figure 3. The three head-to-tail structure formulated in I (Figure 1) is assigned to this isomer on the basis of its n.m.r. spectrum (see Figure 4 and also ref. 6). The complete interpretation of the spectrum has been discussed in detail in ref. 6 and need not be discussed further in the present publication.

The last band eluted from the silver nitrate coated column furnished, as already mentioned above, tridehydro[18]annulene isomer II. This compound analyzed perfectly for a $C_{18}H_{12}$ hydrocarbon and gave cyclooctadecane upon full hydrogenation. It showed an ultraviolet spectrum (see Table I and Figure 2) indicating II to have a highly conjugated system with a main peak at λ_{max} 331 $m\mu$ (ϵ 166,000) (compared with main peak of isomer I at λ_{max} 335 $m\mu$ (ϵ 190,000)). In the infrared spectrum of isomer II, presented in Figure 3, noteworthy are the three strong bands in the 10–12- μ region being split in the latter, as compared to the corresponding similar bands in isomer I and the tetrahydro compound III. The n.m.r. spectrum (taken in this case as well as in those of I and III at 60° for reasons of higher solubility) turned out once more to be very instructive. Thus, the ratio of inner shielded protons appearing at high field⁶ (τ 7.8–8.6) to the outer deshielded protons appearing in the low field (τ 1.7–3.4) was found to be exactly 1:3, in perfect agreement with a tridehydro[18]annulene structure. In the high-field region, two quartets with chemical shifts centered at τ 8.17 and 8.28 and an apparent ratio of 2:1 can be observed (see Figure 3). The quartets are due to the two more similar H^3_a and H^3_b protons and one slightly different H^3_c proton, respectively. The coupling constants due to the splitting of the adjacent H^2 and H^4 protons show values $J_{H^2-H^3} = 12$ c.p.s. and $J_{H^3-H^4} = 15$ c.p.s., in good agreement with isomer I and compound III (see above). The multiplet of peaks in the low-field

region (τ 1.7–3.4) due to the outer protons of II is blurred out because of the nonequivalence of the H^1 , H^2 , and H^4 protons in the three a, b, and c sections of the molecule. It is on the basis of the high-field octet of the inner protons that formula II (see Figure 1) with one head-to-head junction has been assigned to isomer II.

It may be of interest also to note that a comparison of the intensities in the ultraviolet spectrum of the main peak in compounds IV (ϵ 300,000), I (ϵ 190,000), II (ϵ 166,000), and III (ϵ 99,000) indicated that a marked drop in intensity takes place when three acetylenic bonds are substituted for three ethylenic bonds in the C_{18} -membered ring; a further drop in intensity is observed when the C_{18} -membered ring contains four triple bonds.

The proportion of the three dehydroannulenes formed in ten similar couplings (each on a 15-g., 1,5-hexadiyne scale), as obtained after the appropriate chromatographic separations, ranged in *ca.* 70–75% of isomer I, *ca.* 20–25% of isomer II, and *ca.* 5–8% of compound III. The total yield of all three dehydroannulenes based on 1,5-hexadiyne is 2%.

The structure of the three dehydroannulenes I, II, and III has thus been fairly established. However, the unequivocal proof of structure will be given through a three-dimensional X-ray analysis which is currently under investigation by Professor R. Mason in Sheffield.

Experimental¹⁷

Preparation of the Dehydro[18]annulenes I, II, and III. The coupling of 1,5-hexadiyne (in 15-g. batches) and subsequent rearrangement was carried out as described previously, except that the time of coupling was reduced to 2 hr. and the rearrangement was carried out with strong mechanical stirring. The rearranged material obtained from 30 g. of 1,5-hexadiyne concentrated in benzene to a volume of *ca.* 250 ml. was then chromatographed on 3 kg. of Alcoa activated alumina, grade F-20 (supplied by the Aluminum Co. of America, Pittsburgh, Pa.), reactivated by heating at 200–210° for 4 hr. This alumina was found to differ in properties from that used earlier^{3b} (see also part XXXII¹⁸) being much less active, and the separation of triphenylene, C_{18} -dehydroannulenes, and C_{24} -dehydroannulene was less efficient than previously. The fractions containing the cyclic C_{18} compounds (ultraviolet and t.l.c. examinations) were divided into three parts: part I, eluted with pentane-ether (65:35); part II, eluted with pentane-ether (65:35 to 55:45); and part III, eluted with pentane-ether (50:50). Part I contained (in addition to little dehydro[18]annulenes) triphenylene and the yellow substance V, λ_{max} 280 $m\mu$. Part II contained the main bulk of the dehydro[18]annulenes contaminated with the yellow substance V, while part III contained little dehydro[18]annulenes admixed with some dehydro[24]annulene (in addition to a small amount of impurities).

(17) Analyses were carried out in our microanalytical laboratory under the direction of Mr. R. Heller. Ultraviolet spectra were measured on a Cary Model 14 recording spectrophotometer. A Perkin-Elmer Model 137 Infracord equipped with sodium chloride optics was used for the infrared determinations. N.m.r. spectra were taken on an A-60 Varian instrument equipped with a V6040 variable-temperature control, TMS being used as an internal reference.

(18) A. E. Beezer, C. T. Mortimer, H. D. Springall, F. Sondheimer, and R. Wolovsky, *J. Chem. Soc.*, 216 (1965).

(16) (a) E. J. Bailey, D. H. R. Barton, J. Elks, and J. F. Templeton, *J. Chem. Soc.*, 1578 (1962); (b) R. Hanna and G. Ourisson, *Bull. soc. chim. France*, 1945 (1961); (c) F. Sondheimer, Y. Gaoni, L. M. Jackman, N. A. Bailey, and R. Mason, *J. Am. Chem. Soc.*, 84, 4595 (1962).

Part III was evaporated to dryness, dissolved in a small amount of benzene, and rechromatographed on 100 g. of alumina (Alcoa, F-20, reactivated as before) using pentane-ether (65:35) as eluent. The separation between the dehydro[18]annulenes and the dehydro[24]annulenes was now satisfactory (ultraviolet and t.l.c. examination) and the fractions containing the dehydro[18]annulenes were combined with those in part II. The triphenylene present in part I was removed from the mixture by chromatography over silicic acid (Mallinckrodt, analytical reagent, $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ powder of 100 mesh was used). The solution of part I was evaporated to dryness, redissolved in *ca.* 120 ml. of pentane, and chromatographed over a column filled with 100 g. of silicic acid in pentane. While pentane only was used as the eluting solvent, triphenylene came out of the column first (ultraviolet and t.l.c. examinations). The flow of the pentane through the silicic acid was slow; therefore pressure had to be applied on top of the column. When all the triphenylene was eluted, the silicic acid containing the rest of the material was taken out of the column and was extracted with ether. The ether extracts were added to the solution of part II.

To affect separation¹⁹ of the yellow substance V from the dehydro[18]annulenes, the solutions of part II, including those of the repurified dehydro[18]annulenes from part I and part III, were evaporated to dryness, redissolved in *ca.* 200 ml. of pentane, and chromatographed over a column filled with 300 g. of Florisil, 100-200 mesh²⁰ (supplied by NYMCO, Milan, Italy) in pentane. The elution was carried out with pentane only. The dehydro[18]annulenes were eluted out first (ultraviolet and t.l.c. examinations), followed by the yellow substance V. A band of a brown-yellow polymeric material remained on the upper part of the column. The mixture of the dehydro[18]annulenes, free from triphenylene and the yellow substance V, was taken to dryness and redissolved in pentane for separation over a silver nitrate coated column.

Preparation of Silver Nitrate Coated Alumina. A solution of 100 g. of silver nitrate in 500 ml. of distilled water was added to 500 g. of alumina (Merck, acid-washed) in a round-bottomed flask, and the suspension was shaken well. The flask was then connected to a rotating evaporator and the contents was dried under reduced pressure (water pump) with outside heating of a water bath. When the water of the suspension was removed (after *ca.* 1.5 hr.), the contents was transferred into a porcelain dish and further heated in an oven for 2 hr. at a temperature of 100°.

Separation of the Three Dehydro[18]annulenes I, II, and III. A column was filled in pentane with 300 g. of the 20% silver nitrate coated alumina. The mixture of dehydro[18]annulenes in *ca.* 350 ml. of pentane was introduced and the column was eluted with pentane-benzene mixtures ranging in the ratio from 95:5 to 80:20. Fractions of 250 ml. were collected. During the chromatography, three yellow-brown colored,

distinctly separated bands were observed to move down the column. The chromatography was followed by examination of the ultraviolet spectra of the fractions. The first band that came out of the column in fractions 24-36 was eluted with pentane-benzene (95:5). These yellow-red solutions, all with the same typical ultraviolet spectra (maxima at 316 sh, 327, 395, and 383 μ), were combined to yield spectroscopically 31 mg. (0.1%) of *tetradehydro[18]annulene (III)*. Upon evaporation and crystallization from pentane-ether, 25 mg. of crystalline material could be obtained in the form of brick-red rectangular plates, m.p.²¹ 190° dec. The ultraviolet spectrum (as given in Table I) was found to be unchanged upon further recrystallizations from pentane-ether. The compound gave a single spot on t.l.c. examination with a silver nitrate coated plate. The infrared spectrum in KBr (see Figure 3) showed bands at 3.30 (w), 4.60 (w), 4.73 (w), 5.35 (w), 5.48 (w), 5.91 (w), 6.25 (w), 6.57 (w), 6.70 (w), 7.08 (w), 7.19 (w), 7.80 (m), 7.91 (w), 8.21 (w), 8.41 (w), 8.52 (w), 9.13 (w), 10.35 (s), 10.80 (s), 11.33 (s), 13.28 (s), 13.45 (s), and 14.2 (w) μ .

Substance III was soluble in benzene, chloroform, and ether, but only moderately soluble in pentane. It could be kept in the solid state for 1 or 2 days with only very little change. However, crystals that were left for 3 months at room temperature and unprotected from diffuse daylight were decomposed, as evidenced by their turning into an insoluble brown-black material. In solution, *e.g.*, ether, the compound is more stable and could be kept at room temperature for several months, decomposing only to a small extent.

Anal. Calcd. for $\text{C}_{18}\text{H}_{10}$: C, 95.54; H, 4.46. Found²²: C, 95.44; H, 4.52.

Full hydrogenation of III in ethyl acetate with platinum as catalyst yielded cyclooctadecane, identified through vapor phase chromatographic²³ comparison with an authentic sample.

The second band to come out of the column in fractions 56-75 was eluted with pentane-benzene (90:10). The yellow solutions that had similar ultraviolet spectra (maxima at 322, 335, 385, and 399 μ) were combined to yield, spectroscopically, 452 mg. (1.5%) of *tridehydro[18]annulene isomer I*. Evaporation to dryness and crystallization from pentane-ether yielded (in two crops (417 mg. of light brown, rectangular plates, m.p.²¹ 192° dec. The ultraviolet spectrum (as given in Table I) was unchanged on further crystallization and the compound gave only one spot upon t.l.c. examination with a silver nitrate coated plate. The infrared spectrum in KBr (see Figure 3) showed bands at 3.31 (w), 4.64 (w), 4.75 (w), 5.40 (w), 5.50 (w), 5.90 (w), 7.07 (m), 7.57 (w), 7.79 (m), 7.89 (w), 8.18 (w), 8.41 (w), 9.05 (m), 10.01 (w), 10.27 (s), 10.80 (s), 11.82 (s), and 13.12 (s) μ . The solubility properties as well as the stabilities of isomer I in solution or in the solid

(21) The melting points were determined on a Fisher-Johns apparatus and are uncorrected. The block was preheated close to the range of temperature of the melting point and the crystals were placed between glass plates on the block at the desired temperatures. Slow heating of the compounds resulted in their gradual polymerization and could not be used for melting points determination.

(22) For the precautions which were taken during the analysis, *cf.* footnote 6 in part VIII of this series: F. Sondheimer, Y. Amiel, and R. Wolovsky, *J. Am. Chem. Soc.*, **81**, 4600 (1959).

(23) Research Specialties Model 600 instrument with an argon ionization detector was used. The column, 6 ft. \times 0.25 in. o.d., was packed with 5% silicon rubber SE30 on Chromosorb W.

(19) Attempts to separate the yellow substance (λ_{max} 280 μ) V by crystallizations or by repeated rechromatographies of the mixtures on different kinds of alumina, *e.g.*, Alcoa F-20 (basic), Woelm (neutral), or Merck acid-washed, as well as on silicic acid, were unsuccessful.

(20) A proportion of one part of compound to *ca.* 500 parts of Florisil was usually sufficient to effect the separation; however, with Florisil of 60-100 mesh, a proportion of 1 part of compound to *ca.* 1500 parts of adsorbent was found to be necessary.

state were essentially the same as those described already for tridehydro[18]annulene.^{3b}

Anal. Calcd. for C₁₈H₁₂: C, 94.70; H, 5.30. Found²²: C, 94.60; H, 5.37.

Hydrogenation to completion in ethyl acetate in the presence of a platinum catalyst yielded cyclooctadecane, identified as before.

The third band came out in fractions 100–114 and was eluted with pentane–benzene (85:15). The yellow fractions with the same characteristic ultraviolet spectrum (maxima at 318, 331, 340, 387, and 402 m μ) were combined to yield, spectroscopically, 119 mg. (0.5%) of *tridehydro[18]annulene isomer II*. Evaporation to dryness and crystallization from pentane yielded (in two crops) 98 mg. of light brown rectangular plates, m.p.²¹ 200° dec. The crystals looked exactly the same as those obtained from isomer I. The ultraviolet spectrum of II (*cf.* Table I) was unchanged upon further recrystallizations, and the compound gave only one spot on t.l.c. examination with a silver nitrate coated plate. The infrared spectrum in KBr (see Figure 3) showed bands at 3.31 (w), 4.65 (w), 5.76 (w), 5.90 (w), 7.08 (w), 7.13 (w), 7.78 (m), 7.83 (m), 7.94 (w), 8.28 (w), 8.39 (m), 8.60 (w), 8.92 (w), 9.09 (w), 9.36 (w), 10.27 (s), 10.76 (m), 10.86 (s), 11.74 (m), 11.87 (m), 13.26 (s), 14.09 (w), and 14.74 (w) m μ . The solubility properties of isomer II were not much different from those of isomer I; thus it was only moderately soluble in pentane, more soluble in ether, and very soluble in benzene or chloroform. The stability properties were also not markedly different from those of isomer I, though isomer II seemed to be the more stable one in both the solid state and in solution.

Anal. Calcd. for C₁₈H₁₂: C, 94.70; H, 5.30. Found²²: C, 94.77; H, 5.33.

Full hydrogenation of isomer II in ethyl acetate as in the other two cases yielded cyclooctadecane, identified as above.

Thin Layer Chromatographies (t.l.c.). A. Plates. For comparative analytical purposes and for small-scale preparative separations, the conventional 20 × 20 cm. glass plates were used. For rapid analyses (elution time 2–4 min. only) small-scale 7.5 × 2.5 cm. plates (microscopic slides) were used. The larger plates were prepared in the conventional manner and were dried for 40 min. at 120°. The small plates were prepared by spraying evenly a homogeneous slurry prepared from 15 g. of adsorbent and 30 ml. of water, with the aid of a capillary atomizer with wide capillary bore. The coated plates were then dried in an oven for 10–15 min. at 120° and stored in a desiccator over anhydrous CaCl₂.

B. Silver Nitrate Coated Plates. These were prepared in the same way as above with the only exception that instead of water a 20% w./v. silver nitrate aqueous solution was used to prepare the slurry. The dried silver nitrate coated plates were stored as above but kept in the dark.

C. Adsorbents, Eluents, and Developers. Kieselgel G (Merck, Darmstadt) was found to render the best separations and was generally applied. For separations of the three dehydro[18]annulenes, Kieselgel G coated with silver nitrate was found to be most effective. Replacement of Kieselgel G by aluminum oxide G (Merck, Darmstadt) as support for the silver nitrate also sepa-

rated the three dehydro[18]annulenes but produced more elongated spots, in contrast to the sharp round spots obtained with the former. The three dehydro[18]annulenes did not separate on t.l.c. plates prepared without silver nitrate. The eluents used were pentane or pentane–ether mixture²⁴ with uncoated plates and pentane–benzene (95:5 to 85:5) mixture with the silver nitrate coated plates. Uncoated t.l.c. plates were developed by spraying with a permanganate reagent prepared by dissolving 0.5 g. of potassium permanganate in 100 ml. of a saturated solution of cupric acetate in water. The compounds appeared as yellow-green spots on a violet background within 1–2 min. Triphenylene does not react with this reagent; however, plates tested for the latter could be developed with iodine vapors. A yellow-brown spot develops within 3–5 min. Silver nitrate coated plates were developed with a 0.5% ethanolic solution of dichlorofluorescein and illuminated for visualization with an ultraviolet lamp. Alternatively they could be left unprotected from daylight for 2–3 days, whereupon the compounds appeared as black spots on a grey background.

D. R_f Values. (a) *On a 20% Silver Nitrate Coated (Small) Plate.* (i) Developed (once) with pentane–benzene (85:15): compounds I, II, and III showed values of R_f 0.24, 0.14, and 0.30, respectively. (ii) Repeated development (eight times) with pentane–benzene (95:5): compounds I, II, and III gave values of R_f 0.57, 0.34, and 0.68, respectively.

(b) *On Kieselgel G (Small) Plate.* (i). Developed (once) with pentane–ether (95:5): compounds I, II, and III gave values of R_f 0.52, 0.50 and 0.45, respectively; or when developed (once) with pentane–ether (90:10) they showed values of R_f 0.63, 0.62, and 0.56, respectively. (ii). Developed (once) with pentane only: isomer I, triphenylene, yellow compound V, and annulene (IV) rendered values of R_f 0.18, 0.21, 0.12, and 0.20, respectively; when developed four times with pentane only, these compounds showed values of R_f 0.56, 0.63, 0.40, and 0.58, respectively. (Owing to the fact that the thickness of the layers may change on different preparations of plates, the R_f values quoted above signify mainly the relative values between the compounds rather than their absolute values.)

Partial Hydrogenations of the Dehydro[18]annulenes I, II, and III to [18]Annulene (IV). *Tridehydro[18]annulene Isomer I.* I (32 mg.) dissolved in 25 ml. of benzene (thiophene free) was partially hydrogenated in the presence of a 10% palladium on charcoal catalyst as described previously.^{14b} Ultraviolet examination of the benzene solution so obtained revealed that a new peak at 378 m μ had been formed. Careful chromatography over alumina^{14b,18} (Merck, acid washed) rendered fractions of unreacted tridehydro[18]annulene isomer I, followed by those of [18]annulene. The annulene recovered from the latter was found to exhibit the ultraviolet, infrared, and n.m.r. properties as described previously.^{14b,6}

Tridehydro[18]annulene, Isomer II. A solution of 29 mg. of II in 25 ml. of benzene (thiophene free) was

(24) It was found that in many cases better separations could be achieved on silver nitrate coated plates by carrying out repeated elutions with pentane only, rather than performing a single elution with the mixture of solvents. The latter procedure was the faster and for this reason the preferred one.

partially hydrogenated in the presence of a 10% palladium on charcoal catalyst as above. Examination of the ultraviolet spectrum of the benzene solution revealed in this case too that a new peak at 378 $m\mu$ had been formed during the partial hydrogenation process. Chromatography over alumina in the same way as described for isomer I rendered [18]annulene, identity of which was proved again as above.

Tetrahydro[18]annulene (III). III (21 mg.) was dissolved in 25 ml. of benzene (thiophene free) and the solution was subjected to partial hydrogenation in the presence of 15 mg. of palladium catalyst as above. The rate of hydrogen absorption was markedly slower in this case as compared with that of tridehydro[18]annulene isomer I or II. The hydrogenation was interrupted when *ca.* 3 moles of hydrogen was absorbed and a yellow-green color due to the presence of [18]-

annulene was observed. The ultraviolet spectrum of the benzene solution was examined; it showed the presence of a new peak at 378 $m\mu$ that had been formed during the hydrogenation process. Very careful chromatography on alumina (Merck, acid washed) rendered fractions that contained some starting material III followed by fractions with little [18]annulene as evidenced by ultraviolet and t.l.c. comparisons. There could not be detected any traces of a tridehydro[18]-annulene in the chromatography fractions.

Acknowledgments. The author wishes to thank Professor Franz Sondheimer for his interest and encouragement, as well as for many helpful discussions during the course of the present work. Thanks are due also to Dr. Youval Shvo for taking the n.m.r. spectra and to Mrs. Lydia (Groppe) Fischmann for her devoted help in performing the experiments.

Molecular Asymmetry of Olefins. III. Optical Stability of *trans*-Cyclononene and *trans*-Cyclodecene¹

Arthur C. Cope, K. Banholzer, Hannelore Keller, Beverly A. Pawson,²
J. J. Whang, and Hans J. S. Winkler

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received February 8, 1965

Resolution of trans-cyclononene has been accomplished by the scheme employed in the resolution of trans-cyclooctene. It was found that trans-cyclononene racemized spontaneously at room temperature at such a rate that no optical activity could be observed when the olefin was recovered from the pure diastereoisomeric platinum complexes by the procedure which yielded optically active trans-cyclooctene. When the recovery was performed by a fast reaction at room temperature and the rotation of the olefin was measured below 0°, optical activity was observed and rates of racemization could be measured. trans-Cyclodecene that was recovered from pure diastereoisomeric platinum complexes under these conditions was optically inactive.

In the first publication of this series,³ the resolution of *trans*-cyclooctene via a platinum complex containing an optically active amine was reported. The same scheme of resolution has now been applied to *trans*-cyclononene and *trans*-cyclodecene. However, recovery of the olefins with aqueous potassium cyanide under the conditions employed for the recovery of optically active *trans*-cyclooctene afforded racemic olefins. Recovery of *trans*-cyclononene from the platinum complex by rapid reactions followed by immediate cooling to low temperatures afforded optically active, although optically unstable, olefin. Optically active

trans-cyclodecene could not be isolated by this procedure.

The existence of enantiomers of *trans*-cyclononene has been predicted.⁴ From inspection of models, revolution of the plane of the sp^2 -hybridized bonds appeared difficult due to ring strain and nonbonded interactions of the olefinic hydrogen atoms with the hydrogen atoms of the methylene groups across the ring. Increased hindrance to rotation of the ethylenic linkage (such as a reduction in ring size, as in *trans*-cyclooctene) would enhance the optical stability of the olefin. The nonbonded interactions apparent in Stuart-Briegleb models makes it impossible to construct a model of *trans*-cyclononene, even though the *trans*-olefinic bond can be rotated with respect to the rest of the molecule in other types of models. By the use of Barton models, the minimum distance between the nearest hydrogen atoms during the path of least interference to the rotation of the double bond unit in *trans*-cyclononene could be estimated as 1.5 Å.

trans-Cyclononene and *trans*-cyclodecene were prepared by reactions described in the Experimental section. Platinum complexes of the olefins were formed by displacement of ethylene from (+ or -)-*trans*-dichloro(ethylene)(α -methylbenzylamine)plat-

(1) Supported in part by the Army Research Office (Durham) under Grant No. DA-ARO(D)-31-124-G404.

(2) National Institutes of Health Predoctoral Fellow, 1963-1965.

(3) A. C. Cope, C. R. Ganellin, H. W. Johnson, Jr., T. V. Van Auken, and H. J. S. Winkler, *J. Am. Chem. Soc.*, **85**, 3276 (1963).

(4) (a) A. T. Blomquist, L. H. Liu, and J. C. Bohrer, *ibid.*, **74**, 3643 (1952). (b) V. Prelog in "Perspectives in Organic Chemistry," A. Todd, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 129. (c) Molecular asymmetry as stated in this paper refers to the existence of nonsuperimposable enantiomers. *trans*-Cyclic olefins do possess a simple axis of symmetry, however, and would be referred to as dissymmetric in the strictest sense rather than asymmetric (denoting lack of an element of symmetry). For a complete discussion of these terms, see J. W. Wheland, "Advanced Organic Chemistry," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, Chapter 6.