

300-ml. round-bottomed flask equipped with a magnetic stirring bar. The material was dried for 3 days over phosphorus pentoxide in an evacuated desiccator. A total of 150 ml. of anhydrous ethanol was distilled into the flask from sodium ethoxide and diethyl phthalate. The flask was fitted with a condenser and a drying tube and heated under reflux for 42 hours after which most of the ethanol was distilled at atmospheric pressure. The cooled reaction mixture was treated with 6.0 g. of potassium carbonate then diluted with water and extracted with chloroform. The chloroform extracts were dried over magnesium sulfate and flash distilled. Fractional distillation of the residue yielded 1.561 g. (18%) of pure 3-acetoxymethylcyclohexene, b.p. 80–85° (13 mm.), identified by vapor phase chromatography and infrared spectroscopy; 0.289 g. of intermediate, b.p. 85–103° (13 mm.); and 6.877 g. (ca. 65%) of a mixture of *cis*-2-ethoxycyclohexylcarbinyl acetate and monoacetates of *cis*-2-hydroxymethylcyclohexanol.

The 6.877 g. of higher boiling material obtained above was saponified with 3.4 g. of potassium hydroxide in 20 ml. of methanol and 10 ml. of water. Most of the methanol was distilled and the residue was diluted with 10 ml. of water and extracted four times with chloroform. The chloroform was flash distilled and the residue was fractionated to yield 0.807 g. (9% based on *trans*-2-acetoxymethylcyclohexyl brosylate) of *cis*-2-ethoxycyclohexylcarbinol, b.p. 103–105°, n_D^{20} 1.4588; 0.355 g. of intermediate, b.p. 106–135°; and 1.145 g. (14% based on *trans*-2-acetoxymethylcyclohexyl brosylate) of pure *cis*-2-hydroxymethylcyclohexanol, b.p. 135–137° (13 mm.), m.p. 47–48° (lit.¹⁷ m.p. 49–50°).

The infrared spectrum and retention time on vapor phase chromatography of the *cis*-2-ethoxycyclohexylcarbinol obtained above were identical with those of authentic material. A sample of the *cis*-2-ethoxycyclohexylcarbinol was converted to the *p*-nitrobenzenesulfonate which melted at 31–32° undepressed upon mixing with authentic *cis*-2-ethoxycyclohexylcarbinyl *p*-nitrobenzenesulfonate and their infrared spectra in chloroform solution were superimposable.

The Reaction of 3-Acetoxymethylcyclohexene with Acetic Acid in the Presence of *p*-Toluenesulfonic Acid.—A solution of 0.500 g. of 3-acetoxymethylcyclohexene in 15 ml. of 0.1 *M* *p*-toluenesulfonic acid in anhydrous acetic acid was heated under reflux for 30 hours. The reaction mixture was worked up and examined as described for the solvolysis of *trans*-2-acetoxymethylcyclohexyl brosylate in acetic acid. The vapor phase chromatogram of the products showed five peaks which corresponded exactly to the products from the solvolysis of *trans*-2-acetoxymethylcyclohexyl brosylate in acetic acid without added potassium acetate. The product diacetate of 2-hydroxymethylcyclohexanol (ca. 4%) was found to be pure *cis*-2-acetoxymethylcyclohexyl acetate by comparison of its infrared spectrum with that of an authentic sample.

The Reaction of *cis*-2-Acetoxymethylcyclohexyl Acetate in Acetic Acid in the Presence of *p*-Toluenesulfonic Acid.—A solu-

tion of 0.500 g. of *cis*-2-acetoxymethylcyclohexyl acetate in 15 ml. of 0.1 molar *p*-toluenesulfonic acid in anhydrous acetic acid was heated under reflux for 30 hours. Analysis of the products as described previously showed about 8% of 3-acetoxymethylcyclohexene and 90% of *cis*-2-acetoxymethylcyclohexyl acetate of greater than 95% purity. In addition there was a trace of the three compounds noted previously with retention times longer than that of the diacetates of the 2-hydroxymethylcyclohexanols.

The Reaction of the Ethyl Orthoacetate of *cis*-2-Hydroxymethylcyclohexanol with Acetic Acid in the Presence of *p*-Toluenesulfonic Acid.—A solution of 0.8453 g. of the orthoester and 12 ml. of 0.1 *M* *p*-toluenesulfonic acid in anhydrous acetic acid was heated under reflux for 3 hours and worked up as described for the solvolysis of *trans*-2-acetoxymethylcyclohexyl brosylate in acetic acid. The reaction products were analyzed by a combination of vapor phase chromatography and infrared spectroscopy as previously described. The products were 10% of 3-acetoxymethylcyclohexene, 65% of *cis*-2-acetoxymethylcyclohexyl acetate and 25% of *trans*-2-acetoxymethylcyclohexyl acetate.

The Reaction of Cyclohexene and Formaldehyde in Aqueous Sulfuric Acid.²⁴—The following procedure was adapted from the directions of Mikeska and Arundale.¹⁸ In a 1-l. 3-necked flask fitted with a stirrer, condenser and a dropping funnel was placed 150 g. of 50% (by volume) sulfuric acid and 90 g. of paraformaldehyde. A total of 249 g. of cyclohexene was added dropwise with vigorous stirring. After the addition was complete the heterogeneous mixture was heated at 70° for 2 hours. The cooled reaction mixture was neutralized with sodium carbonate and steam distilled. Fractionation of the organic layer yielded 150 g. of cyclohexene and 60 g. (ca. 14% based on total cyclohexene) of impure cyclic formal of *trans*-2-hydroxymethylcyclohexanol, b.p. 193–198° (atm.), n_D^{20} 1.4680–1.4648. The material showed three major peaks on vapor phase chromatography using a 5-foot Carbowax 20M column at 150°. The first eluted component was shown to be cyclohexanol from its retention time and infrared spectrum.

A sample of the impure material obtained above was dissolved in methanol containing 10% by volume of concentrated sulfuric acid and allowed to stand at room temperature. Aliquots were removed from the reaction mixture, neutralized with sodium carbonate and extracted with ether. The ether extracts were evaporated and the residue subjected to vapor phase chromatography. After 4 days it was found that the products consisted of about 80% of pure *trans*-2-hydroxymethylcyclohexanol by comparing the retention time and infrared spectrum of an effluent peak with those of an authentic sample, and 20% of lower boiling materials. The composition of the reaction mixture did not change after 4 days.

(24) The authors are indebted to Mr. Herbert M. Swick for carrying out this experiment.

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

Unsaturated Macrocyclic Compounds. XXVIII.¹

1,2,7,8,13,14-Hexamethyltridehydro-[18]-annulene and 1,2,7,8,13,14-Hexamethyl-[18]annulene

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RECEIVED AUGUST 20, 1962

3-Butyn-2-ol (I) is converted to 3-bromo-1-butyne (II), which on reaction with magnesium in tetrahydrofuran yields 3,4-dimethyl-1,5-hexadiyne (III). Isomerization of the diyne III with potassium *t*-butoxide in *t*-butyl alcohol leads to 3,4-dimethyl-1,3-hexadien-5-yne (IV), as evidenced by the ultraviolet spectrum. Oxidation of the diyne III with cupric acetate in pyridine and subsequent isomerization with potassium *t*-butoxide in *t*-butyl alcohol and benzene gives rise to a mixture of polymethyl-dehydroannulenes, from which 1,2,7,8,13,14-hexamethyltridehydro-[18]annulene (VI) is isolated. Partial hydrogenation of the dehydroannulene VI apparently leads, in very low yield, to 1,2,7,8,13,14-hexamethyl-[18]annulene (VIII), although this substance was not obtained in pure form.

It has been shown that 1,5-hexadiyne by oxidative coupling and subsequent base isomerization may be converted to a series of fully conjugated cyclic polyene-polyynes (dehydroannulenes),² which on partial hydrogenation yield the corresponding conjugated cyclic polyenes (annulenes).³ It was of interest to utilize this type of synthesis for the preparation of substituted

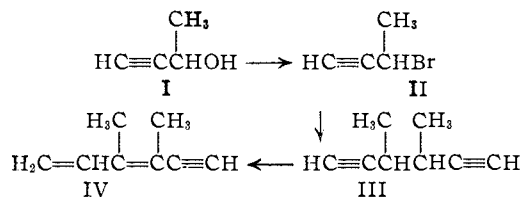
dehydroannulenes and annulenes, in order that the effect of the substituents on the physical and chemical properties might be studied. In the present paper we report the synthesis of 1,2,7,8,13,14-hexamethyltridehydro-[18]annulene (VI) and of 1,2,7,8,13,14-hexamethyl-[18]annulene (VIII), the former substance, but not the latter, being isolated in pure form. These compounds differ from the previously described tridehydro-[18]annulene² and [18]annulene³ in possessing six methyl substituents, most probably directed "outside" the ring as shown.

(1) For Part XXVII, see L. M. Jackman, F. Sondheimer, Y. Amiel, D. A. Ben-Efraim, Y. Gaoni, R. Wolovsky and A. A. Bothner-By, *J. Am. Chem. Soc.*, in press.

(2) F. Sondheimer and R. Wolovsky, *ibid.*, **84**, 260 (1962).

(3) F. Sondheimer, R. Wolovsky and Y. Amiel, *ibid.*, **84**, 274 (1962).

The monomer required for the present work was the previously unknown 3,4-dimethyl-1,5-hexadiyne (III), which was prepared from the commercially available 3-butyn-2-ol (I) *via* 3-bromo-1-butyne (II). The conversion of the alcohol I to the bromide II by means of phosphorus tribromide in the presence of pyridine has



been described before.⁴ We have found that the bromide II thus obtained is impure, even after careful distillation, and a pure sample was isolated only after chromatography on alumina. However, for convenience the crude bromide was utilized directly for the next step, which involved treatment with magnesium in tetrahydrofuran solution. The corresponding reaction with propargyl bromide had previously been shown to lead to a mixture of 1,5-hexadiyne and the allene 1,2,4,5-hexatetraene.⁵ The coupling of the bromide II was found to result in a mixture of substances, from which the required diyne III was obtained by conversion to the silver derivative and regeneration with sodium cyanide solution. The structure of the resulting liquid diyne III, which presumably consists of a mixture of racemic and *meso* forms, is based on the elemental composition, the fact that the infrared spectrum indicated the presence of terminal acetylene but no allene groupings, and the absence of appreciable absorption in the ultraviolet. The presently described synthesis of the diyne III proceeds only in low yield, but is convenient since it involves only two steps from a readily available starting material.

It has been found previously that 1,5-hexadiyne is rearranged smoothly to 1,3-hexadien-5-yne by means of potassium *t*-butoxide,⁶ a reaction which was applied to the cyclic polymers of this diyne in order to obtain dehydroannulenes.² To ascertain whether 3,4-dimethyl-1,5-hexadiyne (III) undergoes a similar rearrangement, this branched diyne was boiled with a saturated solution of potassium *t*-butoxide in *t*-butyl alcohol, aliquots being withdrawn at intervals and the ultraviolet spectra were determined. It was found that a sharp single maximum at 261 m μ (in pentane) was developed, undoubtedly due to the formation of 3,4-dimethyl-1,3-hexadien-5-yne (IV). The calculated value for the position of the maximum of this substance is 262 m μ , since 1,3-hexadien-5-yne shows $\lambda_{\text{max}}^{\text{isooctane}}$ 252 m μ (single peak)⁶ and each of the two methyl substituents is expected to cause a bathochromic shift of 5 m μ .⁷ The optimum yield of the dienyne IV, estimated spectroscopically, was *ca.* 20%, and was reached after a reaction time of 45 minutes; no attempt was made, however, to isolate IV in pure form.

3,4-Dimethyl-1,5-hexadiyne (III) was oxidized with cupric acetate in pyridine⁸ under conditions similar to those employed by us with 1,5-hexadiyne.² The resulting product appeared to be mainly cyclic, since it showed α,γ -diacetylene bands but only a very weak acetylenic hydrogen band in the infrared. However,

it was not found possible to isolate any pure cyclic compound at this stage, even after careful chromatography on alumina. This is not surprising, since each of the various cyclic coupling products (*e.g.*, the cyclic trimer V) would be expected to be present as a mixture of stereoisomers in view of the existence of several asymmetric centers.

The total coupling product from the diyne III in subsequent experiments was rearranged directly by being boiled in benzene solution with a saturated solution of potassium *t*-butoxide in *t*-butyl alcohol for 45 minutes. Chromatography of the resulting mixture on alumina and ultraviolet spectral examination of representative fractions showed that the same type of mixture of dehydroannulenes had been formed as had been obtained by coupling and subsequent rearrangement of 1,5-hexadiyne.² However, the separation between the various conjugated compounds was not as clear-cut as in the desmethyl series (see Experimental section for details),⁹ and only hexamethyltridehydro-[18]annulene (VI) was obtained in pure form. The yield of this substance was *ca.* 1%, based on the diyne III.

The dehydroannulene VI, evidently formed from the cyclic trimer V by a rearrangement analogous to that leading from the monomer III to the dienyne IV, crystallized as brown-red prisms which decomposed on attempted melting point determination. The ultraviolet spectrum (in benzene), which showed four maxima at 336, 351, 396 and 412 m μ (ϵ 93,700, 146,000, 14,900 and 15,200, respectively), is reproduced in Fig. 1 and compared there with that of tridehydro-[18]annulene [$\lambda_{\text{max}}^{\text{benzene}}$ 329, 342, 391, 407 and 441 m μ (ϵ 94,600, 155,000, 12,000, 15,200 and 1,100, respectively)].² It can be seen that the spectra of the two substances are very similar (only the low-intensity 441 m μ maximum in tridehydro-[18]annulene finds no counterpart in VI), the introduction of the six methyl groups causing a bathochromic shift in the positions of the maxima by *ca.* 7 (± 2) m μ . On the other hand, the ultraviolet spectrum of compound VI differed considerably from that of tetrahydro-[24]annulene (high intensity maxima in benzene at 333 and 350 m μ , but no maxima at higher wave lengths),² of penta-dehydro-[30]annulene (main maxima in benzene at 400 m μ)² or of hexadehydro-[36]annulene (main maximum in benzene at 407 m μ).² These spectral comparisons, as well as the ultraviolet spectrum of the partial hydrogenation product described below, strongly suggests that the conjugated substance under discussion possesses the trimeric structure. This assignment was supported by a molecular weight determination, carried out by the thermistor-drop technique in methylene chloride,^{10,11} which gave a value (370) intermediate between the molecular weight of compound VI (312) and of octamethyltetrahydro-[24]annulene (417); however, the substance was not completely in solution, a fact which would tend to give a high result and which therefore indicates the trimeric rather than the tetrameric structure to be correct.

We believe the hexamethyltridehydro-[18]annulene most probably possesses the unstrained planar structure

(9) The difficulty experienced in attempting to isolate the higher poly-methyldehydroannulenes in pure form may also be due to the fact that the likelihood of more than one isomer of any dehydroannulene being formed is greater in the methyl series than in the unsubstituted series. Different locations for the methyl groups are possible, and in the higher members the tendency for all the methyl groups to be directed "outside" the ring (*i.e.*, to be attached to the *cis*-double bonds, rather than to the *trans*-double bonds or to the single bonds) will presumably be reduced.

(10) B. R. Y. Iyengar, *Rec. trav. chim.*, **73**, 789 (1954).

(11) This determination was carried out through the courtesy of Dr. V. M. Clark and Mr. G. Purdy, Cambridge University, to whom we express our thanks.

(4) (a) M. T. Rogers and M. B. Panish, *J. Am. Chem. Soc.*, **77**, 3684 (1955); (b) M. Gaudemar, *Ann. chim. (Paris)*, [13] **1**, 181 (1956).

(5) L. Miginiac, *Compt. rend.*, **247**, 2156 (1958); see also L. Groizeleau-Miginiac, *ibid.*, **248**, 1190 (1959).

(6) F. Sondheimer, D. A. Ben-Efraim and Y. Gaoui, *J. Am. Chem. Soc.*, **83**, 1682 (1961).

(7) R. B. Woodward, *ibid.*, **64**, 72 (1942).

(8) C. J. G. Eglinton and A. R. Galbraith, *J. Chem. Soc.*, 889 (1959).

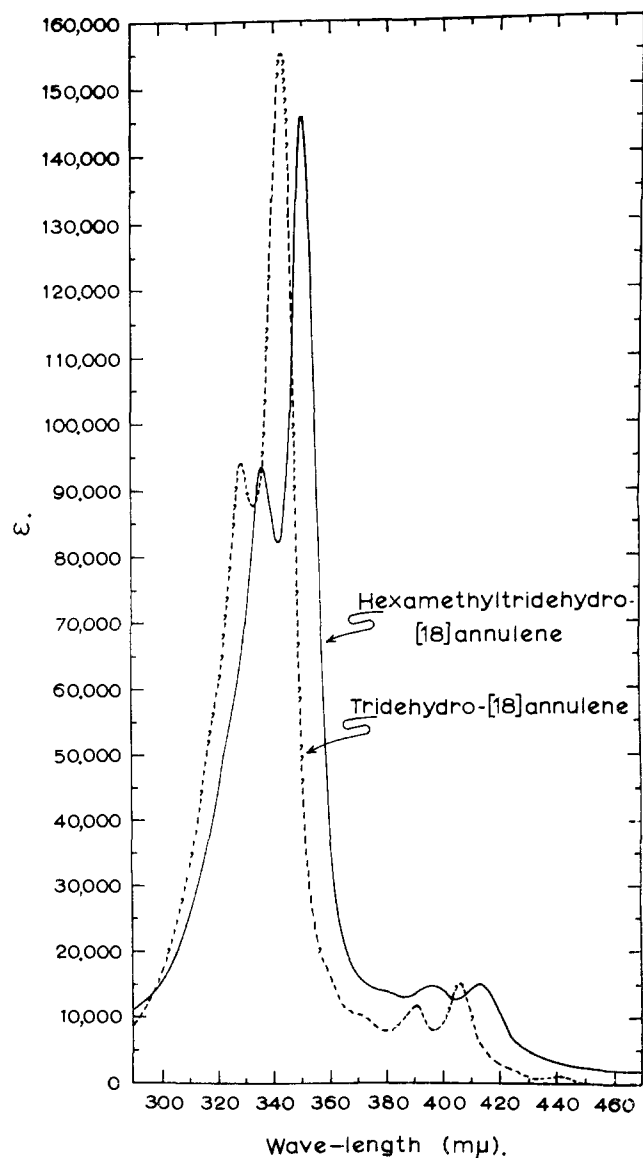


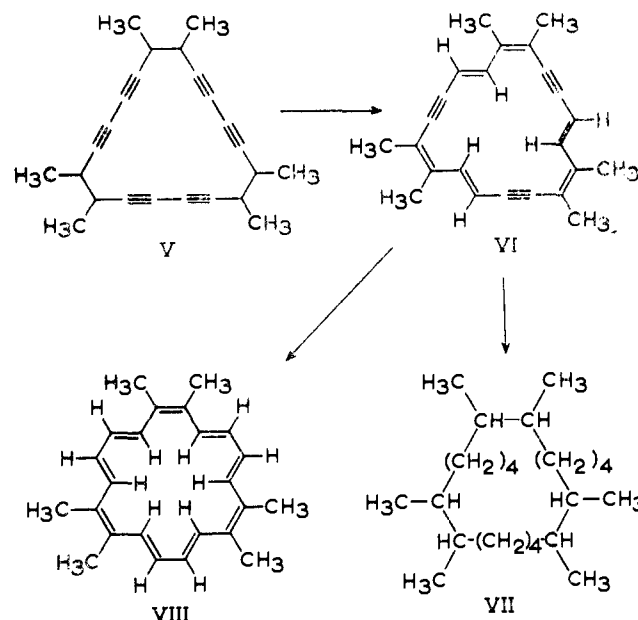
Fig. 1.—Ultraviolet absorption spectra (in benzene) of hexamethyltridehydro[18]annulene (VI) (solid line) and of tridehydro[18]annulene (broken line).²

VI with the methyl groups attached to the *cis*-double bonds and consequently directed outside the ring. Other possible structures have methyl groups directed inside the ring, and could presumably not be planar in view of severe steric overcrowding. Were this the case, it would be unlikely for the ultraviolet spectrum to correspond so closely to that of tridehydro-[18]annulene. Moreover the infrared spectrum of hexamethyltridehydro-[18]annulene showed a strong band at 10.60 μ , indicative of the presence of disubstituted *trans*-double bonds conjugated with acetylene,¹² as in VI.

The nuclear magnetic resonance (n.m.r.) spectrum¹³ of hexamethyltridehydro-[18]annulene (VI) in deuteriochloroform solution showed a well defined band at 7.40 τ , due to the protons of the methyl groups (unfortunately no bands corresponding to the other protons could be detected, presumably because of the low concentration of the solution). Evidently the

(12) See J. L. H. Allan, G. D. Meakins and M. C. Whiting, *J. Chem. Soc.*, 1874 (1955), and references cited there.

(13) The n.m.r. spectrum, obtained through the courtesy of Prof. L. M. Jackman (Imperial College of Science, London), was determined with a Varian V4300 spectrometer operating at 60 Mc./sec. Tetramethylsilane (0.5%) was employed as an internal reference and the band position was obtained by the side-band technique.



protons of the methyl groups are deshielded by a ring current, since the protons of "in-chain" methyl groups in carotenoids (including acetylenic analogs) absorb at considerably higher field (7.95–8.15 τ).¹⁴ Hexamethyltridehydro-[18]annulene, like tridehydro-[18]annulene,¹ therefore appears to be aromatic, in keeping with the facts that the substance complies with Hückel's rule and that it is presumably planar.

The hexamethyl-compound VI, while being considerably less soluble in most solvents than tridehydro-[18]annulene, resembled the latter in stability. Thus compound VI could be kept practically unchanged for a considerable time in solution at room temperature, or in the solid state at -15° . However, the substance showed no unusual stability characteristics, and gradually decomposed on being allowed to stand in the solid state at room temperature.

Hexamethyltridehydro-[18]annulene (VI) readily absorbed the theoretical amount of hydrogen on hydrogenation in ethyl acetate over a platinum catalyst. The reaction, however, did not proceed stereospecifically, and the product consisted of a mixture of stereoisomers of 1,2,7,8,13,14-hexamethylcyclooctadecane (VII) from which no pure isomer could be separated.

Finally, the partial hydrogenation of hexamethyltridehydro-[18]annulene (VI) to hexamethyl[18]annulene (VIII) was investigated. The reaction was carried out in benzene solution over a 10% palladium-charcoal catalyst and was interrupted when *ca.* 4 molar equivalents of gas had been absorbed. As in the case of the partial hydrogenation of tridehydro-[18]annulene, which under these conditions had led to [18]annulene in fair yield,³ no break in the rate of hydrogen uptake was observed after the theoretical amount had been absorbed. Ultraviolet examination of the resulting solution showed the typical maxima of unchanged starting material (*ca.* 30% recovery). However, careful chromatography on alumina yielded yellow fractions containing hexamethyl-[18]annulene (VIII), eluted from the column directly after unchanged VI. The structure assigned to the annulene VIII is based on the ultraviolet spectra of these fractions, which showed maxima (in benzene) at 391 and 469 $m\mu$ (relative optical densities, 1:0.115). By comparison, the main ultraviolet maxima of [18]annulene (in

(14) M. S. Barber, J. B. Davis, L. M. Jackman and B. C. L. Weedon, *J. Chem. Soc.*, 2870 (1960). We are indebted to Prof. Jackman for an interesting discussion regarding the n.m.r. spectrum of hexamethyltridehydro-[18]annulene (VI).

benzene) are at 378 and 456 μ (relative optical densities, 1:0.096).³ A bathochromic shift of 13 μ in the positions of the maxima appears to be associated with the introduction of the six methyl groups. Again, the methyl groups in hexamethyl-[18]annulene are presumably directed outside the ring, as in VIII; were the methyl groups directed inside the ring, the compound would be far from planar and the ultraviolet spectral characteristics would presumably be very different from those of [18]annulene.

It is to be noted that the yield of hexamethyl-[18]annulene (VIII) was very low, being of the order of 0.3% (determined spectroscopically, the ϵ -value of the main maximum of VIII being assumed to be the same as that of [18]annulene³). The yield could not be improved by employing a Lindlar lead-poisoned palladium-calcium carbonate catalyst¹⁵ for the hydrogenation, or by allowing different amounts of hydrogen to be taken up. In addition, the hydrogenation reaction appeared to give rise to other substances, and the separation of the annulene VIII from these or from unchanged VI was not clear-cut. For these reasons it was not found possible to obtain compound VIII completely pure, even in solution.

Hexamethyl-[18]annulene (VIII), like [18]annulene, should be an aromatic compound. Interestingly, the hexamethyl derivative VIII proved to be considerably less stable than the unsubstituted compound,³ dilute solutions in pentane-ether decomposing comparatively rapidly on being allowed to stand at room temperature without protection from diffuse daylight.

Experimental¹⁶

3-Bromo-1-butyne (II).—Dry pyridine (1 cc.) was added to 822 g. (3.04 moles) of phosphorus tribromide, previously cooled to ca. -15° in an ice-salt-bath, moisture being excluded. A solution of 30 cc. of pyridine in 578 g. (8.26 moles) of 3-butyne-2-ol (I) (L. Light and Co.; previously dried over potassium carbonate and distilled through a Vigreux column) was then added dropwise during 4 hr., with stirring and continued cooling. The cooled mixture was stirred for another 1 hour, and ice and water were then added. The mixture was extracted well with ether and the ether layers were washed with water and sodium bicarbonate solution. The organic extract was dried, the ether was distilled off through a 60-cm. Vigreux column, and the brown-black residue was distilled through the same column. The resulting crude 3-bromo-1-butyne (455 g., 41.4%) was obtained as a colorless liquid, b.p. 34–44° (83 mm.), n_D^{20} 1.4680; found: Br, 54.82; infrared bands (chloroform) at 3.02(s) and 4.71(w) μ (terminal acetylene) as well as at 5.91(m) μ (carbonyl).¹⁷ Careful redistillation did not lead to a pure product.

A sample of the pure bromide II was obtained by chromatography of 4 g. of the crude material on 150 g. of alumina and developing the column with pentane. The solvent was removed from each fraction by distillation through a Vigreux column. The fractions which did not show a carbonyl band in the infrared¹⁷ were combined and redistilled. The resulting pure bromide II was a colorless liquid, b.p. 94–96° (756 mm.), n_D^{20} 1.4748; infrared bands (chloroform) at 3.03(s) and 4.72(w) μ (terminal acetylene), no carbonyl band in the 5.7–6.0 μ region [reported: b.p. 50° (170 mm.),^{4b} n_D^{25} 1.4766^{4a}; no elemental analysis given^{4a,b}].

Anal. Calcd. for C₄H₅Br: C, 36.12; H, 3.79; Br, 60.08. Found: C, 35.88; H, 3.89; Br, 59.92.

3,4-Dimethyl-1,5-hexadiyne (III).—Magnesium (394 g., 16.2 moles) was covered with 1.25 l. of tetrahydrofuran (previously dried and redistilled over sodium), 0.2 g. of mercuric chloride and 5 g. of crude 3-bromo-1-butyne (II) were added, and the mixture was heated in a water-bath under a reflux condenser until an exothermic reaction started. The bath was removed and a solution of 793 g. of crude II (total, 6.0 moles) in 150 cc. of tetra-

hydrofuran was then added dropwise during 2 hr. with continuous stirring, the exothermic reaction causing the mixture to boil steadily throughout the addition. The mixture was stirred for another 2.5 hr. while immersed in a water-bath kept at 40°, and was then allowed to stand at room temperature for 16 hr. The resulting solid mass was cooled in ice, ice and water were added, the mixture was filtered, and the filtrate was well extracted with ether. The ether extract was washed with water, dried over sodium sulfate and distilled through a 60-cm. Vigreux column. Five fractions with the following properties were collected: (i) ca. 2 l., b.p. 35–60°; (ii) 230 cc., b.p. 60–73°; (iii) 125 cc., b.p. 73–118°; (iv) 8 cc., b.p. 118–122°; (v) 12 cc., b.p. 40° (70 mm.)–62° (55 mm.). Infrared examination showed that fractions ii–v contained the diyne III (terminal acetylene bands at ca. 3.03(s) and 4.72(w) μ) as well as allenic material (weak allene band at ca. 5.09 μ) and solvent.

The fractions ii–v were combined, diluted with an equal volume of ethanol, and a 75% (w./v.) aqueous silver nitrate solution was added gradually with stirring until no further precipitate separated. The supernatant liquid was decanted off from the precipitated silver derivative, and the latter was washed by decantation successively with ether, ethanol and water. The precipitate was then boiled for 2 hr. with an 80% (w./v.) aqueous sodium cyanide solution under a condenser cooled with Dry Ice-acetone. The mixture was cooled, extracted with ether, and the organic layer was washed with water. The ether solution was dried and the solvent was removed through a Vigreux column. Distillation of the residue under reduced pressure then yielded 18.5 g. (5.8%) of 3,4-dimethyl-1,5-hexadiyne as a colorless liquid, b.p. 49–52° (80 mm.); infrared bands (chloroform) at 3.03(s) and 4.72(m) μ (terminal acetylene), only trace of a band at 5.09 μ (allene); no appreciable absorption in the ultraviolet; negative Beilstein test for halogen. Redistillation through a small Vigreux column gave an analytical specimen, b.p. 50–52° (80 mm.), n_D^{20} 1.4405, unchanged infrared spectrum.

Anal. Calcd. for C₈H₁₀: C, 90.50; H, 9.50. Found: C 90.15; H, 9.41.

Isomerization of 3,4-Dimethyl-1,5-hexadiyne (III) to 3,4-Dimethyl-1,3-hexadien-5-yne (IV).—A solution containing 170 mg. of the diyne III and 30 cc. of a saturated solution of potassium *t*-butoxide in *t*-butyl alcohol was gently boiled under reflux in nitrogen, moisture being excluded. Aliquots were withdrawn at intervals, diluted with pentane, washed well with water, dried, diluted to known volume with pentane, and the ultraviolet spectra were determined against pentane. All the aliquots showed a single sharp maximum at 261 μ due to the dienyne IV. The yields are based on the assumption that the ϵ -value of the maximum of pure IV is 30,000 (the unsubstituted 1,3-hexadien-5-yne shows $\epsilon_{\text{max}}^{261\text{m}\mu}$ 25,500⁸).

Time, min.	7	15	30	45	60	90
Yield, %	3.4	7.4	14.5	20.5	16.7	13.3

Oxidative Coupling of 3,4-Dimethyl-1,5-hexadiyne (III).—A solution of 15 g. of the diyne III in 100 cc. of pyridine was added to a suspension of 225 g. of neutral cupric acetate monohydrate in 1.4 l. of pyridine (commercial grade, previously distilled over sodium hydroxide). The vigorously stirred mixture was heated to 65° by means of a water-bath during ca. 15 minutes, and was then stirred at this temperature for 4 hr. The mixture was cooled, allowed to stand overnight at room temperature, filtered, and the solid was washed well with benzene, the washings being kept separately. The filtrate was evaporated to small volume under reduced pressure (outside temperature not above 50°), the residue was combined with the benzene washings, and was then washed with dilute hydrochloric acid and water. The dried extract on evaporation to dryness under reduced pressure yielded 12.7 g. of a brown semi-solid residue, the infrared spectrum of which (in chloroform) showed α,γ -diacetylene bands at 4.42(w) and 4.62(w) μ , but only a very weak acetylenic hydrogen band at 3.02 μ .

The crude coupled material (760 mg.) with similar properties, from a previous experiment, was chromatographed on 165 g. of alumina. A series of crystalline colorless or slightly yellow products was obtained by evaporation of the fractions eluted with pentane-ether (17:3) to pure ether. These consisted of cyclic polymers of the diyne III (*e.g.*, V), since the infrared spectra (KBr disks) of representatives showed α,γ -diacetylene bands at ca. 4.42(w) and 4.62(w) μ , but no acetylenic hydrogen band at ca. 3.03 μ . However, none of these products (which decomposed on attempted m.p. determination) appeared to be homogeneous, nor could a pure substance be obtained by crystallization.

(15) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

(16) All chromatograms were carried out with Alcoa activated alumina, grade F-20 (Aluminum Co. of America, Pittsburgh, Pa.). Ultraviolet spectra were taken on a Unicam model S.P. 500 as well as on a Cary model 14 recording spectrophotometer. Infrared spectra were measured on a Perkin-Elmer "Infracord" recording spectrophotometer (sodium chloride optics). Analyses were performed in our microanalytical laboratory under the direction of Mr. Erich Meier.

(17) Cf. J. H. Wotiz, F. A. Miller and R. J. Palchak, *J. Am. Chem. Soc.*, **72**, 5055 (1950); B. Hampel, *Z. physik. Chem. (Frankfurt)*, **13**, 123 (1937).

1,2,7,8,13,14-Hexamethyltridehydro[18]annulene (1,2,7,8,13,14-Hexamethyl-1,3,7,9,13,15-cyclooctadecahexaene-5,11,17-triyne) (VI) and Higher Polymethyl-dehydroannulenes.—The crude coupling product (12.7 g.; derived from 15 g. of the diyne III) described in the preceding experiment was dissolved in 900 cc. of benzene, and the solution was divided into three equal parts. Each part was added to 300 cc. of a saturated solution of

potassium *t*-butoxide in *t*-butyl alcohol, heated to boiling during *ca.* 5 minutes and then allowed to boil gently under reflux for 45 minutes, moisture being excluded. The resulting black-brown mixtures were cooled in ice, combined, and poured on ice-water. The aqueous layer was washed with benzene, and the combined benzene extracts were then washed well with water and dried. The resulting brown solution [main ultraviolet maximum at 349 $m\mu$ (in benzene), due to the dehydroannulene VI] was evaporated to *ca.* 70 cc. and poured on a column of 2.5 kg. of alumina, prepared with pentane. The column was washed with pentane, various mixtures of pentane-ether, and finally with ether.

Pentane-ether (7:3 to 13:7) eluted orange-red solutions, all of which in the ultraviolet showed the main maxima at *ca.* 329 and 343 $m\mu$ and the subsidiary maxima at *ca.* 390 and 405 $m\mu$ (against pentane) of the dehydroannulene VI; the spectroscopic yield was 245 mg. (1.7% based on the diyne III). These fractions on combination, evaporation to small volume and cooling produced 85 mg. of crystalline VI in two crops. Rechromatography of the mother liquors and subsequent crystallization furnished another 43 mg. (total yield, 128 mg.; 0.9% based on the diyne III). The resulting hexamethyltridehydro-[18]annulene (VI) formed brown-red prisms, which decomposed on attempted m.p. determination; $\lambda_{\max}^{\text{isoctane}}$ 249, 329, 343, 390 and 406 $m\mu$ (ϵ 27,200, 96,100, 148,500, 14,100 and 14,700, respectively); $\lambda_{\max}^{\text{CH}_2\text{Cl}_2}$ 251, 334, 348, 395 and 411 $m\mu$ (ϵ 26,500, 95,500, 145,000, 14,200 and 14,500, respectively); $\lambda_{\max}^{\text{benzene}}$ 336, 351, 396 and 412 $m\mu$ (ϵ 93,700, 146,000, 14,900 and 15,200, respectively) (see Fig. 1). The infrared spectrum (KBr disk) showed bands at 3.32(w), 3.42(w), 3.50(w), 4.65(w), 6.33(w), 6.50(w), 7.84(m), 8.08(m), 9.13(w), 9.95(w), 10.15(w), 10.60(s), 11.39(w) and 12.09(m) μ . A benzene solution was dark red-brown when concentrated and yellow-orange when dilute. The solubility in methylene chloride at 20° was *ca.* 5 mg./cc. The homogeneity of the substance was demonstrated by the fact that the ultraviolet spectrum was unchanged on recrystallization, and that careful rechromatography gave fractions with identical ultraviolet spectra.

Anal. Calcd. for $\text{C}_{24}\text{H}_{24}$: C, 92.26; H, 7.74. Found: C, 91.80; H, 7.75.

After most of the dehydroannulene VI had been eluted from the column, pentane-ether (13:7) eluted orange-red fractions which showed ultraviolet maxima (against pentane) at *ca.* 333 and 348 $m\mu$, but no further maxima at higher wave lengths. These probably contain 1,2,7,8,13,14,19,20-octamethyltridehydro-[24]annulene, since tetradehydro[24]annulene shows $\lambda_{\max}^{\text{isoctane}}$ 324 and 340 $m\mu$, no maxima at higher wave lengths² (bathochromic shift, 8–9 $m\mu$). However no pure substance could be obtained from these fractions, and rechromatography indicated that they were admixed with VI as well as with the more complex dehydroannulene(s) described directly below.

Finally, elution with pentane-ether (3:2) to pure ether gave red fractions which showed ultraviolet maxima (against pentane) in the 380–400 $m\mu$ region. These were combined, evaporated to small volume, diluted with ethanol and cooled. The resulting dark red plates (365 mg.), which decomposed on attempted m.p. determination, showed $\lambda_{\max}^{\text{CH}_2\text{Cl}_2}$ 409 $m\mu$; $\lambda_{\max}^{\text{benzene}}$ 411 $m\mu$; acetylene band at 4.65(w) μ in the infrared (KBr disk). This material apparently consists of 1,2,7,8,13,14,19,20,25,26-decamethylpentadecahydro-[30]annulene and/or 1,2,7,8,13,14,19,20,25,26,31,32-dodecamethylhexadecahydro-[36]annulene, since pentadecahydro-[30]annulene shows main $\lambda_{\max}^{\text{benzene}}$ 400 $m\mu$ ² (bathochromic shift, 11 $m\mu$), and hexadecahydro-[36]annulene shows $\lambda_{\max}^{\text{benzene}}$ 407 $m\mu$ ² (bathochromic shift, 4 $m\mu$). Rechromatography of this crystalline material indicated it to be inhomogeneous, the ultraviolet spectra of representative fractions not being identical.

1,2,7,8,13,14-Hexamethylcyclooctadecane (VII).—A solution of 20 mg. of hexamethyltridehydro-[18]annulene (VI) in 100 cc. of ethyl acetate was stirred in hydrogen over *ca.* 50 mg. of a pre-reduced platinum catalyst at 29° and 754 mm. Uptake ceased after *ca.* 30 minutes, when 18.9 cc. (11.8 molar equivalents) had been absorbed. The catalyst was removed, washed with ethyl acetate, and the solvent was evaporated. The resulting mixture of stereoisomers of 1,2,7,8,13,14-hexamethylcyclooctadecane formed a colorless semi-solid mass, soluble in ether but insoluble in ethanol. It was not possible to obtain a pure isomer by crystallization or by chromatography on alumina. Attempts to determine the molecular weight of the mixture of isomers by mass spectroscopy (carried out through the courtesy of Dr. D. Samuel, Isotope Department, Weizmann Institute of Science) led to no significant result.

1,2,7,8,13,14-Hexamethyl[18]annulene (1,2,7,8,13,14-Hexamethyl-1,3,5,7,9,11,13,15,17-cyclooctadecanonaene) (VIII).—A suspension of 25 mg. of a 10% palladium-charcoal catalyst in 10 cc. of thiophene-free benzene was stirred in hydrogen at 30° and 756 mm. until equilibrium was reached. A solution of 38 mg. of hexamethyltridehydro-[18]annulene (VI) in 60 cc. of benzene was added, and stirring in hydrogen was continued. After 16 minutes, 12.2 cc. (4 molar equivalents) of hydrogen had been absorbed and the reaction was terminated; no break in the rate of hydrogen uptake was observed during the reaction. Removal of the catalyst and ultraviolet examination of the resulting orange solution against ether showed the typical maxima of unchanged starting material (29% recovery, determined spectroscopically), but an additional shoulder at *ca.* 383 $m\mu$ was apparent. The solution was concentrated to *ca.* 4 cc. under reduced pressure, and was then chromatographed on a column of 200 g. of alumina, prepared with pentane. The column was washed with pentane and then with various mixtures of pentane-ether. Fractions containing unchanged starting material (as shown by the typical ultraviolet maxima) were eluted with pentane-ether (7:3). In the subsequent fractions, eluted with pentane-ether (7:3 to 3:2), an ultraviolet maximum at *ca.* 383 $m\mu$ (against ether) due to hexamethyl-[18]annulene (VIII) appeared, this band becoming more intense in successive fractions while the bands due to unchanged starting material became less pronounced; the fractions in which the 383 $m\mu$ maximum was intense in addition exhibited a maximum of lesser intensity at *ca.* 461 $m\mu$. The yield of the annulene VIII based on the 383 $m\mu$ maximum was *ca.* 0.3% [the ϵ -value of this maximum in the pure substance is assumed to be the same (*ca.* 300,000) as that of the main maximum of [18]annulene²].

The fractions showing the pronounced 383 $m\mu$ band were combined, evaporated and rechromatographed on a column of 40 g. of alumina. The fractions containing the annulene VIII least contaminated with other ultraviolet-absorbing materials were yellow in color and were eluted with pentane-ether (7:3). They showed $\lambda_{\max}^{\text{isoctane}}$ 383 and 461 $m\mu$ (relative optical densities, 1:0.107); $\lambda_{\max}^{\text{benzene}}$ 391 and 469 $m\mu$ (relative optical densities, 1:0.115); in addition small bands due to unchanged starting material as well as subsidiary maxima or inflections at *ca.* 315, 363, 433 and 448 $m\mu$ (in benzene) were apparent. Only traces of a yellow-orange material was obtained on evaporation of these fractions.

A chromatographic fraction containing the annulene VIII in pentane-ether (7:3) was allowed to stand at room temperature without protection from diffuse daylight, the optical density of the 383 $m\mu$ maximum being determined at intervals. After 3 days *ca.* 65% of the annulene remained, after 5 days *ca.* 50% remained, after 10 days *ca.* 30% remained, and after 16 days the 383 $m\mu$ maximum was no longer apparent.