(65%). Anal. Caled. for C₁₈H₂₂O₆: C, 61.5; H, 6.5; mol. wt., 334. Found: C, 61.5; H, 6.5; mol wt., 333. The sirup dissolved in hot water to form a solution from

which a mixture of *cis*- and *trans*-hexahydroterephthalic acids was isolated. WILMINGTON, DELAWARE

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

Unsaturated Macrocyclic Compounds. IV. The Oxidation of Terminal Diacetylenes to Macrocyclic Tetraacetylenes

By F. Sondheimer, Y. Amiel and R. Wolovsky

RECEIVED JULY 1, 1957

The scope of the cyclization reaction of terminal diacetylenes, previously carried out with octa-1,7-diyne (Ia), has been investigated. Nona-1,8-diyne (Ib) and hepta-1,6-diyne (Id) give the corresponding cyclic tetraacetylenes IIb and IId, respectively, the yields becoming better as the ring size decreases. In addition compounds derived by linear coupling result. These linear types of substances are the sole identified products when the reaction is performed with deca-1,9-diyne (Ic) and hexa-1,5-diyne (Ie). The parallel a-diacetylene rods in cyclotetradeca-1,3,8,10-tetrayne (IId) are very close to each other. The substance consequently exhibits unusual physical properties, which are discussed.

The coupling of two molecules of octa-1,7-divne (Ia) through oxidation with oxygen in the presence of cuprous chloride and ammonium chloride to yield cyclohexadeca-1,3,9,11-tetrayne (IIa) besides linear products was described in the previous paper of this series.¹ This appears to be one of the few reactions in which two molecules of a symmetrical difunctional compound condense at both ends to give a carbocyclic large ring. Other examples of this type of reaction are the pyrolysis of heavy metal salts of aliphatic terminal dicarboxylic acids,^{2a} treatment of the corresponding dinitriles with a sodium alkyl-anilide^{2b} or of the diketenes with tertiary amines,^{2c} all of which lead eventually to macrocyclic diketones derived from two molecules of the starting material in addition to the cyclic monomeric monoketones. Into this category also fall the acyloin condensation of diethyl hexahydrophthalate to produce what is probably an eight-membered di-acyloin^{2d} and the reaction of certain terminal dibromoalkylbenzenes with sodium or lithium phenyl to give large ring hydrocarbons incorporating phenyl groups.^{2e-h} It was of interest to investigate the generality of the cyclization reaction of terminal diacetylenes, especially in order to find out if cyclic tetraacetylenes of type II could be obtained in which the two α -diacetylene chains are sufficiently close for electronic interaction to occur. In the present paper we describe the results obtained by submitting the four aliphatic diacetylenes Ib, Ic, Id and Ie to the coupling reaction.3

All the reactions were carried out by bubbling oxygen through a mixture of the diacetylene, cu-

(1) For Part III, see F. Sondheimer and Y. Amiel, THIS JOURNAL, 79, 5817 (1957).

(2) (a) L. Ruzicka, et al., Helv. Chim. Acta, 11, 496, 670 (1928);
13, 1152 (1930); 17, 78 (1934); (b) K. Ziegler and A. Lüttringhaus, Ann., 511, 1 (1934); (c) A. T. Blomquist and R. D. Spencer, THIS JOURNAL, 70, 30 (1948); (d) A. C. Cope and E. C. Herrick, *ibid.*, 72, 983 (1950); (e) W. Baker, et al., J. Chem. Soc., 27 (1945); 200, 1114, 1118 (1951); (f) H. Steinberg and D. J. Cram, THIS JOURNAL, 74, 5388 (1952); (g) E. D. Bergmann and Z. Pelchowicz, *ibid.*, 75, 4281 (1953); (h) see also C. J. Brown and A. C. Farthing, Nature, 164, 915 (1949); J. Chem. Soc., 3261, 3265 (1953).

(3) For a preliminary communication, see Y. Amiel, F. Sondheimer and R. Wolovsky, *Proc. Chem. Soc.*, 22 (1957). See also G. Eglinton and A. R. Galbraith (*Chemistry & Industry*, 737 (1956)) for an independent investigation into the coupling of higher terminal diacetylenes to give cyclic poly-acetylenes. prous chloride and ammonium chloride in aqueous ethanol acidified with hydrochloric acid, at 55°. The products were best purified by chromatography on alumina. The next higher homolog to the previously studied Ia was nona-1,8-diyne (Ib) (readily prepared from 1,5-dibromopentane and sodium acetylide in liquid ammonia)4 and was found to give three products. The least polar was a crystalline chlorine containing substance C₁₈H₂₂Cl₄, obtained in 5% yield, which was apparently not acetylenic (infrared) but showed high intensity absorption maxima at 228 and 235 m μ in the ultraviolet; its structure is now under investigation. Next in order of polarity was a hydrocarbon (2% yield), $C_{18}H_{20}$, m.p. 212°, the infrared spectrum of which showed bands at 2239 and 2138 cm.⁻¹ (disubstituted diacetylene) but not at ca. 3300 or 2100 cm.⁻¹ (lack of terminal acetylene).¹ It thus seems to be cyclic, and it was shown to be the cyclic dimer, cycloöctadeca-1,3,10,12-tetrayne (IIb), through full hydrogenation to cycloöctadecane (IIIb). Lastly, the linear dimer, octadeca-1,8,10,17-tetrayne (IVb), m. p. 22° , was obtained in *ca*. 60% yield; its structure was confirmed by the infrared spectrum (presence of terminal acetylene as well as disubstituted α -diacetylene) and by hydrogenation to *n*-octadecane (Vb). No linear tetramer VIb could be isolated and it must have been present in only small amounts if at all.

The next higher homolog, deca-1,9-divne (Ic),⁵ on being coupled under the usual conditions no longer yielded the cyclic dimer in appreciable amounts. Besides ca. 30% of a chlorine-containing substance, the linear dimer, eicosa-1,9,11,19-tetrayne (IVc), converted to n-eicosane (Vc) by full hydrogenation, was formed in 60% yield. In addition the linear tetramer, tetraconta-1,9,11,19,21,29,31,39-octayne (VIc) could be isolated in quite small yield (3%); its structure was established through hydrogenation to n-tetracontane (VIIc). The fact that in the case of Ib and Ic very little or none of the linear tetramers is obtained is doubtlessly due to the increasing insolubility of the dimers (type IV) in the aqueous ethanol employed as the carbon chain is increased.

(5) W. M. Lauer and W. J. Gensler, ibid., 67, 1171 (1945).

⁽⁴⁾ A. L. Henne and K. W. Greenlee, THIS JOURNAL, 67, 484 (1945).





We next investigated the coupling of hepta-1,6diyne (Id),⁴ containing one less methylene group than the previously studied Ia.1 This reaction led to four different products, separated by chromatography on alumina. The first, as usual, was a chlorine-containing substance as yet unidentified. The second (26%) yield) was the linear dimer, tetradeca-1,6,8,13-tetrayne (IVd), hydrogenated to n-tetradecane (Vd). The third substance, produced in 12% yield, was shown to be the cyclic dimer, cyclotetradeca-1,3,8,10-tetrayne (IId), since it contained only α -diacetylene and no terminal acetylene groupings (infrared, silver nitrate test), since it had the formula $(C_7H_6)_n$ and since full hydrogenation gave cyclotetradecane (IIId) identified with an authentic sample. The most polar substance (18% yield) was the linear tetramer, octacosa-1,6,8,13,15,20,22,27-octayne (VId), converted by hydrogenation to *n*-octacosane (VIId).

The smallest diacetylene investigated, hexa-1,5-diyne (dipropargyl) (Ie),6 on oxidative coupling gave two chlorine-containing compounds, 28% of the linear dimer dodeca-1,5,7,11,-tetrayne (IVe) and 20% of the linear tetramer tetracosa-1,5,7,-11,13,17,19,23-octayne (VIe). The structures of the last two substances are based on the determination of acetylenic hydrogen by titration against silver nitrate⁷ and on the hydrogenation to *n*-dodecane (Ve) and n-tetracosane (VIIe), respectively. It is not too surprising that none of the cyclic dimer cyclododeca-1,3,7,9-tetrayne (IIe) could be isolated from this reaction, as such a substance would require the α -divne rods to be "bent" and no strainless model can be constructed. An unusually large amount of insoluble polymeric material was obtained from the reaction and it is not impossible that IIe was formed but polymerized spontaneously or during the work-up.

The smallest cyclic compound of type II for which a molecular model can be constructed from "Catalin" models is cyclotetradeca-1,3,8,10-tetrayne (IId), the one obtained in highest yield. A picture of the model is reproduced in Fig. 1 and compared with models of cyclohexadeca-1,3,9,11tetrayne (IIa)¹ (Fig. 2) and of cycloöctadeca-1,3,10,12-tetrayne (IIb) (Fig. 3). The model of IId, which is quite strainless, shows the two α diacetylene rods to be very close to each other and considerable electronic interaction might be expected. On the other hand, the α -diacetylene groupings in the other two cycles IIa and IIb are reasonably far apart and these compounds should show more or less normal properties (in constructing the models, the assumption has been made that the diacetylene functions are as far apart from each other as possible). In actual fact the substance IId is much less stable than the other two and on being heated decomposes explosively at $115-120^{\circ}$ with the copious formation of carbon-like material. By comparison, the cyclic substances IIa and IIb show normal melting points above 150° .⁸

Another difference between IId on the one hand and IIa and IIb on the other is shown by the ultraviolet data. In Fig. 4 the ultraviolet spectra of the three cyclic tetraacetylenes are presented and compared with the spectrum of tetradeca-6,8diyne (VIII) (the coupling product of 1-heptyne),⁹ containing an isolated disubstituted α -diacetylene chromophore. As can be seen, the spectra of the two cyclic compounds IIa and IIb are very similar to that of the acyclic model VIII, the three substances all showing maxima at 226–227, 239–240 and 253–254 m μ and minima at 233–234 and 249– 250 m μ . Only a gradual decrease in the depth of the minima in passing from the model VIII to IIb to IIa can be noticed. A striking difference is



shown by the spectrum of the smallest cyclic compound, IId, in which the highest wave length maximum is displaced to 263 m μ and the highest wave length minimum to 258 m μ . The two α diacetylene rods in compounds of type II are therefore sufficiently far apart for no appreciable interference to occur (as judged by the ultraviolet spectrum) when held apart by penta- and tetramethylene bridges at each end, but are so close when separated by trimethylene bridges that marked electronic interaction occurs. A similar phenomenon has been observed by Cram, *et al.*, in the case of the paracyclophanes of type IX. In

(8) It is interesting to note that whereas the cyclic compounds IIa and IIb are less polar than the corresponding acyclic compounds IVa and IVb (as would be expected in view of the absence of the acidic acetylenic hydrogen atoms in the macrocyclic compounds), the substance IId rather surprisingly is *more* polar than the corresponding linear compound IVd.

(9) V. Grignard and Tchéoufaki, Compt. rend., 188, 357 (1929).

⁽⁶⁾ R. A. Raphael and F. Sondheimer, J. Chem. Soc., 120 (1950).
(7) G. Eglinton and M. C. Whiting, *ibid.*, 3052 (1953).





Fig. 3.

these, the ultraviolet spectra are normal when n = 4 or more but the spectra of IX, n = 3, and of IX, n = 2, are anomalous, with the maxima displaced to higher wave lengths.^{10a} The cyclic tetraacetylene IId is the first purely aliphatic hydrocarbon in which this type of non-classical interaction between adjacent unsaturated systems undoubtedly occurs.¹¹

(10) (a) Cf. D. J. Cram, N. L. Allinger and H. Steinberg, THIS JOURNAL, **76**, 6132 (1954); (b) D. J. Cram and N. L. Allinger, *ibid.*, **78**, 2518 (1956).

(11) It is probable that the anomalous spectra of 1,4-dihydrobenzene derivatives of type i and ii (in which the distance between the un-



saturated groupings appears to be about the same as in the tetraacetylene IId) is due to a similar effect [K. Bowden and E. R. H. Jones, J. Chem. Soc., 52 (1946); E. A. Braude, E. R. H. Jones, F. Sondheimer and J. B. Toogood, *ibid.*, 607 (1949); J. C. Lunt and F.



Fig. 4.—Ultraviolet absorption spectra of cyclic tetraacetylenes in isoöctane. The ϵ value of the open-chain model at the bottom has been doubled (to give the value for two α -diacetylene groupings), that of IIb (n = 5) has been increased by 300, that of IIa (n = 4) by 550 and that of IId (n = 3) by 650.

The possibility was mentioned by Cram and Allinger^{10b} that a compound of type X may tautomerize to a cyclobutadiene structure such as XI when n = 4 or 3 since very little decrease in entropy would be involved in such a change. No such transformation was found to occur with Xa, but the behavior of Xb has not been studied since the



Sondheimer, *ibid.*, 3361 (1950); P. D. Bartlett and E. S. Lewis, THIS JOURNAL, **72**, 1005 (1950); D. J. Cram and H. Steinberg, *ibid.*, **73**, 5691 (1951); S. L. Emerman and J. Meinwald, J. Org. Chem., **21**, 375 (1956); E. R. H. Jones, G. H. Mansfield and M. C. Whiting, J. Chem. Soc., 4073 (1956)]. latter is as yet unknown. A similar valency tautomerism might occur with the two tetraacetylenes IIa and IId to give a polycyclic structure of type XII or XIII. That in fact the cyclic compounds exist in the tetraacetylene form is conclusively proved by their infrared and ultraviolet spectra.

Since an α -diacetylene chain and the carbon substituents at either end (>C—C=C-C=C-C<) form a rigid straight six-carbon rod, the cyclic dimer cyclotetradeca-1,3,8,10-tetrayne (IId) can be considered as a cyclohexane in which two opposite bonds have been elongated by the insertion of α diacetylene groupings. Thus, like cyclohexane, IId can exist either in the chair form XIV as pictured in Fig. 1 or in the boat form XV. The two



structures can be differentiated since only the chair form will have a center of symmetry. In fact the crystalline tetraacetylene IId by X-ray methods was found to have a center of symmetry (see Experimental) and therefore, like cyclohexane, exists in the chair form.

Finally we would like to draw attention to the fact that a number of the linear dimers IV and linear tetramers VI in the solid state are photosensitive and their surfaces become covered with insoluble bright red, pink, blue or green polymers. This phenomenon has been observed with other α -diacetylenes¹² and the mechanism has been discussed.¹⁸ On the other hand, the cyclic acetylenes do not show this behavior (they slowly become yellow and then brown on being allowed to stand in the solid state, like other highly unsaturated substances), perhaps because the α -diacetylene groupings in the comparatively rigid frameworks cannot become oriented correctly for the polymerization to occur. From the practical standpoint it is advisable to store all of the polyacetylenes in solution in the cold, in which state they are comparatively stable.

The new cyclization method involving the oxidative coupling of terminal diacetylenes, although it gives rather low yields, makes available for the first time highly unsaturated large-ring compounds in one step from readily available starting materials. Other aspects of the reaction and various transformations of the interesting cyclic polyacetylenes are now being investigated.

Acknowledgments.—We are indebted to Mrs. E. Breuer of the Department of X-Ray Crystallography of this Institute for determining the crystallographic constants of cyclotetradeca-1,3,-

(12) Cf., J. B. Armitage, C. L. Cook, N. Entwistle, E. R. H. Jones and M. C. Whiting, J. Chem. Soc., 1998 (1952).

(13) F. Bohlmann and E. Inhoffen, Ber., 89, 1276 (1956).

8,10-tetrayne and to Prof. V. Prelog of the Eidg. Technische Hochschule, Zürich, for a sample of cyclotetradecane.

Experimental¹⁴

Oxidation of Nona-1,8-diyne (Ib) to Cycloöctadeca-1,3,-10,12-tetrayne (IIb) and Octadeca-1,8,10,17-tetrayne (IVb). —A solution of 5 g. of nona-1,8-diyne (Ib)⁴ in 10 cc. of ethanol was added to a mixture of 10 g. of cuprous chloride and 16 g. of annonium chloride in 42.5 cc. of water containing 0.1 cc. of concd. hydrochloric acid. The mixture was heated to 55° and oxygen was then bubbled in, with vigorous stirring, a condenser kept at ca. -40° by means of Dry Ice-acetone being used to prevent loss of the diacetylene. After 5 hr. at 55° the product was isolated with benzene. The total product (4.9 g.) was chromatographed on 200 g. of alumina. This procedure yielded three substances. The first (0.25 g., 5% yield by weight) was eluted with petroleum ether; it was a chlorine-containing substance, m.p. 143-145°, λ_{max} . 228 and 235 m μ (ϵ 14,000 and 13,000, respectively).

Anal. Caled. for C₁₈H₂₂Cl₄: C, 56.87; H, 5.79; Cl, 37.34. Found: C, 57.04; H, 5.66; Cl, 37.29.

The second substance (0.10 g., 2%) also eluted with petroleum ether proved to be cycloöctadeca-1,3,10,12-tetrayne (IIb); after crystallization from ether it formed plates, m.p. 210-212°; λ_{max} 227, 239 and 254 m μ (e 680, 670 and 470, respectively); μ_{max} 2239 and 2138 cm.⁻¹ (disubstituted α -diacetylene).

Anal. Caled. for C₁₆H₂₀: C, 91.47; H, 8.53. Found: C, 91.47; H, 8.75.

The last substance (2.87 g., 58%) was eluted with petroleum ether-benzene (9:1); it was octadeca-1,8,10,17tetrayne (IVb) and after crystallization from pentane showed m.p. 21-22°, n^{26} p 1.5119, ν_{max} 3300 and 2101 cm.⁻¹ (terminal acetylene) and 2237 and 2131 cm.⁻¹ (disubstituted α -diacetylene). In light the compound gradually became blue.

Anal. Caled. for C₁₈H₂₂: C, 90.70; H, 9.30. Found: C, 90.18; H, 9.02.

Cycloöctadecane (IIIb).—Cycloöctadeca-1,3,10,12-tetrayne (IIb) (50 mg.) dissolved in 10 cc. of dioxane was shaken over 50 mg. of platinum oxide in hydrogen at atmospheric pressure and room temperature until the uptake of gas stopped. One crystallization of the product from ethanol yielded 41 mg. of cycloöctadecane, m.p. 71-72°, no C-CH₃ band at *ca*. 1380 cm.⁻¹ in the infrared¹⁶ (reported^{2a} m.p. 72°).

n-Octadecane (Vb).—Hydrogenation of 50 mg. of octadeca-1,8,10,17-tetrayne (IVb) in 10 cc. of dioxane over 50 mg. of platinum oxide, followed by sublimation, yielded 45 mg. of *n*-octadecane, m.p. 27-28°; the m.p. was undepressed on admixture with an authentic sample (m.p. 28°).

Oxidation of Deca-1,9-diyne (Ic) to Eicosa-1,9,11,19tetrayne (IVc) and Tetraconta-1,9,11,19,21,29,31,39-octayne (VIc).—The oxidation of 5 g. of deca-1,9-diyne (Ic)⁶ was carried out exactly as described above for nona-1,8-diyne (Ib). The total product (4.9 g.) was chromatographed on 200 g. of alumina, whereby three different substances were obtained. The first (1.51 g., 30% by weight), eluted with petroleum ether, was a liquid chlorine-containing substance, b.p. 80-81° (0.2 mm.). The second, also eluted with petroleum ether, proved to be eicosa-1,9,11,19tetrayne (IVc) (2.97 g., 60%); after crystallization from petroleum ether it showed m.p. $30-31^{\circ}$; λ_{max} 226, 240 and $254 \text{ m}\mu$ (ϵ 400, 390 and 240, respectively); ν_{max} 3300 and 2102 cm.⁻¹ (terminal acetylene) and 2238 and 2135 cm.⁻¹ (disubstituted α -diacetylene). In light the compound became blue and then pink.

(14) Melting points and boiling points are uncorrected. All chromatographs were done with Alcoa activated alumina, grade F-20 (Aluminum Co. of America, Pittsburgh, Pa.). Infrared spectra were measured in chloroform solution with a Perkin-Elmer model 12C single beam spectrophotometer with sodium chloride prism. Ultraviolet spectra were determined in isoöctane solution on a Unicam model S.P. 500 spectrophotometer. We are indebted to Dr. S. Pinchas of this Institute for the infrared data and to Mr. Erich Meier for the microanalyses.

(15) Cf. N. Sheppard and D. M. Simpson, Quart. Revs. (London), 7, 19 (1953).

Anal. Calcd. for C₂₀H₂₆: C, 90.16; H, 9.84. Found: C, 89.92; H, 9.67.

The last substance, eluted with petroleum ether-benzene (1:1), was the linear tetramer VIc (0.146 g., 3%), which after crystallization from petroleum ether exhibited m.p. 59-61°; $\lambda_{max} 226$, 240 and 254 m μ (1270, 1230 and 760, respectively); $\nu_{max} 3305$ and 2101 cm.⁻¹ (terminal acetylene) and 2240 and 2136 cm.⁻¹ (disubstituted α -diacetylene).

Anal. Calcd. for $C_{40}H_{50}$: C, 90.50; H, 9.50. Found: C, 90.64; H, 9.59.

n-Eicosane (Vc) was obtained by hydrogenating 100 mg. of eicosa-1,9,11,19-tetrayne (IVc) in 7 cc. of dioxane over platinum oxide. After crystallization from ethanol it showed m.p. 36-37° (reported¹⁶ m.p. 36.7°). *n*-Tetracosane (VIIc).—Hydrogenation of 60 mg. of tetracosa-1,9,11,19,21,29,31,39-octayne (VIc) in 6 cc. of dioxane

n-Tetracosane (VIIc).—Hydrogenation of 60 mg. of tetracosa-1,9,11,19,21,29,31,39-octayne (VIc) in 6 cc. of dioxane over platinum oxide and crystallization of the product from ethanol gave 48 mg. of *n*-tetracosane, m.p. 80-81° (reported¹⁷ m.p. 80.5-81°).

Oxidation of Hepta-1,6-diyne (Id) to Cyclotetradeca-1,3,8,10-tetrayne (IId), Tetradeca-1,6,8,13-tetrayne (IVd) and Octacosa-1,6,8,13,15,20,22,27-octayne (VId),—The oxidation of 5 g. of hepta-1,6-diyne (Id) was carried out as described above for nona-1,8-diyne (Ib), except that the time of reaction was only 1.5 hr. (this was found to give superior results to the usual 5-hr. reaction time). A bulky insoluble gummy mass separated during the reaction. The product was isolated with benzene as usual and after evaporation of the solvent was separated into a part soluble in petroleum ether and another part soluble in petroleum ether-benzene (2:1). A small amount of material insoluble in the latter solvent pair was discarded. The two solutions were chromatographed separately on alumina and yielded together four different substances. The first (0.25 g., 5% by weight) was a liquid chlorine-containing substance which was eluted with petroleum ether. The second (1.28 g., 26%) was the linear dimer IVd, eluted with petroleum ether-benzene (4:1); it showed b.p. 110-111° (0.7 mm.), m.p. ca. -5° ; $\lambda_{max} 226$, 240 and 254 m μ (e 540, 510 and 440, respectively); $\nu_{max} 3300$ and 2102 cm.⁻¹ (terminal acetylene) and 2236 and 2142 cm.⁻¹ (disubstituted α -diacetylene).

Anal. Caled. for C14H14: C, 92.31; H, 7.69. Found: C, 91.98; H, 7.67.

The third product, eluted with petroleum ether-benzene (2:1), was cyclotetradeca-1,3,8,10-tetrayne (IId). After crystallization from ethanol it weighed 0.59 g. (12%) and formed transparent wedges which on being heated decomposed explosively at *ca*. 115–120° with the copious formation of fluffy black flakes; $\lambda_{\rm max}$ 226, 238 and 263 m μ (ϵ 610, 590 and 370); $\nu_{\rm max}$ 2236 and 2148 cm.⁻¹ (disubstituted α -diacetylene), but not at *ca*. 3300 and 2100 cm.⁻¹ (absence of terminal acetylene). The substance gave no precipitate with a 5% solution of silver nitrate in 95% ethanol.

Anal. Caled. for C₁₄H₁₂: C, 93.33; H, 6.66. Found: C, 93.50; H, 6.50.

The crystallographic constants of IId were found to be: a = 8.80 Å., b = 8.05 Å., c = 8.30 Å., $\beta = 112^{\circ}24'$, space group P2₁/n. The calculated density for $Z_1 = 2$ is 1.10. The space group consequently demands a molecular center of symmetry.

The last substance, eluted with petroleum ether-benzene (1:1), was the linear tetramer VId. After crystallization from petroleum ether it weighed 0.88 g. (18%) and showed m.p. $60-61^\circ$; $\lambda_{max} 226$, 240 and 254 mµ (ϵ 1150, 1060 and 800, respectively); $\nu_{max} 3300$ and 2104 cm.⁻¹ (terminal acetylene) and 2233 and 2146 cm.⁻¹ (disubstituted α -diacetylene). On being allowed to stand in the light in the solid state it slowly becomes green and then blue.

(17) W. H. Carothers, J. W. Hill, J. E. Kirby and R. A. Jacobson, THIS JOURNAL, 52, 5279 (1930). Anal. Caled. for C₂₈H₂₆: C, 92.77; H, 7.23. Found: C, 92.50; H, 7.34.

Cyclotetradecane (IIId).—Cyclotetradeca - 1,3,8,10 - tetrayne (IId) (100 mg.) in 20 cc. of acetic acid was hydrogenated at atmospheric pressure and room temperature over platinum oxide until uptake stopped. One crystallization from methanol gave pure cyclotetradecane (82 mg.), m.p. 51-52°, undepressed on admixture with an authentic specimen (m.p. 52-53°) (reported¹⁸ m.p. 52-53°). *n*-Tetradecane (Vd).—Tetradeca-1,6,8,13-tetrayne (IVd) (330 mg.) in 10 cc. of acetic acid was hydrogenated over

n-Tetradecane (Vd).—Tetradeca-1,6,8,13-tetrayne (IVd) (330 mg.) in 10 cc. of acetic acid was hydrogenated over platinum oxide as usual. Passage of the product through alumina in petroleum ether gave 310 mg. of *n*-tetradecane, m.p. 5.5°, b.p. 250-251° (754 mm.) (reported¹⁹ m.p. 5.5°, b.p. 251° (760 mm.)). *n*-Octacosane (VIId).—Octacosa-1,6,8,13,15,20,22,27octayne (VId) (50 mg.), dissolved in a mixture of 10 cc. of dioxane and 10 cc. of acetic acid. was shaken in hydrogen

n-Octacosane (VIId).—Octacosa-1,6,8,13,15,20,22,27octayne (VId) (50 mg.), dissolved in a mixture of 10 cc. of dioxane and 10 cc. of acetic acid, was shaken in hydrogen over a platinum oxide catalyst until absorption was completed. Crystallization of the product from ethanol gave 43 mg. of n-octacosane, m.p. 60-61° (reported¹⁹ m.p. 61.4°).

bleted. Crystallization of the product from ethanol gave 43 mg. of *n*-octacosane, m.p. 60–61° (reported¹⁹ m.p. 61.4°). Oxidation of Hexa-1,5-diyne (Ie) to Dodeca-1,5,7,11tetrayne (IVe) and Tetracosa-1,5,7,11,13,17,19,23-octayne (VIe).—The oxidation of 5 g. of hexa-1,5-diyne (dipropargyl) (Ie)⁶ was carried out as described above for nona-1,8-diyne (Ib), except that the time of reaction was only 2 hr. The product was isolated with benzene, as previously. The part (3.5 g.) soluble in petroleum ether was chromatographed on 160 g. of alumina. The insoluble part (1.2 g.) was a brown polymeric powder. The chromatogram yielded four products. The first two, eluted with petroleum ether, were chlorine-containing liquid substances. The third, eluted with petroleum ether-benzene (9:1), was the linear dimer IVe; after crystallization from pentane it weighed 1.38 g. (28%) and showed m.p. 99–100°; λ_{max} 226, 240 and 254 m μ (ϵ 530, 460 and 300, respectively); ν_{max} 3300 and 2104 cm.⁻¹ (terminal acetylene) and 2239 and 2133 cm.⁻¹ (disubstituted α -diacetylene). In light the compound becomes pink.

Anal. Calcd. for $C_{12}H_{10}$: C, 93.46; H, 6.54; acetylenic H, 1.31. Found: C, 93.90; H, 6.41; acetylenic H (by titration against silver nitrate),⁷ 1.30.

The fourth substance, eluted with petroleum ether-benzene (1:1) and benzene, was the linear tetramer VIc, which after crystallization from petroleum ether weighed 0.99 g. (20%) and showed m.p. 167-168° dec., λ_{max} 229, 240 and 254 mµ (ϵ 1580, 1310 and 880, respectively); ν_{max} 3300 and 2104 cm.⁻¹ (terminal acetylene) and 2239 and 2137 cm.⁻¹ (disubstituted α -diacetylene). In light the compound becomes red.

Anal. Calcd. for C₂₄H₁₈: C, 94.11; H, 5.88; acetylenic H, 0.65. Found: C, 93.73; H, 5.79; acetylenic H,⁷ 0.64.

n-Dodecane (Ve).—Dodeca-1,5,7,11-tetrayne (IVe) (1 g.) dissolved in 25 cc. of acetic acid was hydrogenated over 0.25 g. of platinum oxide until uptake of gas ceased. The product (0.91 g.) showed b.p. $215-216^{\circ}$ (762 mm.), m.p. -10° (reported for *n*-dodecane¹⁹ b.p. 216.2° (760 mm.), m.p. -9.6°).

n-Tetracosane (VIIe).—Tetracosa-1,5,7,11,13,17,19,23octayne (VIe) (100 mg.), suspended in 25 cc. of ethanol, was hydrogenated over platinum oxide at atmospheric pressure and room temperature until absorption ceased. Crystallization of the product from methanol gave 86 mg. of *n*-tetracosane, m.p. 49-50° (reported¹⁹ m.p. 51.1°).

REHOVOTH, ISRAEL

(18) L. Ruzicka, M. Stoll, H. W. Huyser and H. A. Bockenoogen, Helv. Chim. Acta, 13, 1152 (1930).

(19) P. J. Garner and J. H. Beynon in "Chemistry of Carbon Compounds," Vol. IA, edited by E. H. Rodd, Elsevier Publishing Co., Houston, Texas, 1951, p. 228.

⁽¹⁶⁾ F. Krafft, Ber., 19, 2218 (1886).