

<i>i</i> -C ₄ H ₉	Cyclohexylmethylamino	1	<i>p</i>	90-94	262-264	C ₂₀ H ₃₁ O ₃ N ₂ Cl	9.26	9.36	383	385
<i>i</i> -C ₄ H ₉	Furfurylamino	1	<i>p</i>	Oil	244-247	C ₁₈ H ₂₃ O ₄ N ₂ Cl	9.66	9.39	367	363
<i>i</i> -C ₄ H ₉	Benzylamino	1	<i>p</i>	103-106	240-242	C ₂₀ H ₂₆ O ₃ N ₂ Cl	9.41	9.56	377	384
<i>i</i> -C ₄ H ₉	NH(CH ₂) ₃ N(CH ₃) ₂	1	<i>p</i>	Oil	226-228	C ₁₈ H ₃₀ O ₃ N ₃ Cl	9.54	9.31	372	368
<i>n</i> -C ₆ H ₁₁	NHC ₂ H ₅	1	<i>p</i>	Oil	206-208	C ₁₈ H ₂₅ O ₃ N ₂ Cl	10.78	11.01	329	332
<i>n</i> -C ₆ H ₁₁	NHC ₄ H ₉	1	<i>p</i>	Oil	244-246	C ₁₈ H ₂₉ O ₃ N ₂ Cl	9.93	9.91	357	359
<i>n</i> -C ₆ H ₁₁	NHC ₄ H ₉ (iso)	1	<i>p</i>	57-59	205-208	C ₁₈ H ₂₉ O ₃ N ₂ Cl	9.93	9.85	357	358
<i>n</i> -C ₆ H ₁₁	N(C ₂ H ₅) ₂	1	<i>p</i>	Oil	138-142	C ₁₈ H ₂₉ O ₃ N ₂ Cl	9.93	9.81	357	353
<i>n</i> -C ₆ H ₁₁	Morpholino	1	<i>p</i>	88-91	162-164	C ₁₈ H ₂₇ O ₄ N ₂ Cl	9.56	9.72	371	373
<i>n</i> -C ₆ H ₁₃ (CH ₃)CH	N(C ₂ H ₅) ₂	1	<i>p</i>	Oil	110-114	C ₂₁ H ₃₅ O ₃ N ₂ Cl	8.89	8.70	399	394
<i>n</i> -C ₆ H ₁₃ (CH ₃)CH	Morpholino	1	<i>p</i>	Oil	112-115	C ₂₁ H ₃₅ O ₄ N ₂ Cl	8.59	8.89	413	420
<i>n</i> -(C ₂ H ₅) ₂ NCH ₂ CH ₂	NHC ₄ H ₉ (iso)	1	<i>p</i>	Oil	187-191	C ₁₉ H ₃₃ O ₃ N ₂ Cl ₂	16.78	16.40	422	416
<i>n</i> -(C ₂ H ₅) ₂ NCH ₂ CH ₂	N(C ₂ H ₅) ₂	1	<i>p</i>	18-22	193-195	C ₁₉ H ₃₃ O ₃ N ₃ Cl ₂	16.78	17.02	422	426
<i>n</i> -(C ₂ H ₅) ₂ NCH ₂ CH ₂	Morpholino	1	<i>p</i>	Oil	151-154	C ₁₉ H ₃₁ O ₄ N ₃ Cl ₂	16.26	16.61	436	441

^a Most of these bases form crystalline hydrates. However, the anhydrous form is reported in this column. Since they crystallize with difficulty, some of these compounds reported as oils may crystallize on long standing. ^b Reported² m.p. of base 101-102°, m.p. of hydrochloride 218°. ^c Reported² m.p. of base 59-60°, m.p. of hydrochloride 186-187°. ^d Reported^{4,5} m.p. of base 115°, m.p. of hydrochloride 211°. ^e B.p. 152-156° at 20 μ.

acidified with anhydrous hydrochloric acid. The precipitated salt was recrystallized from 99% isopropyl alcohol to yield 12.8 g. (89%) of the isobutyl ester of *p*-(β-diethylaminopropionylamino)-benzoic acid hydrochloride as white crystals, m.p. 150-152°.

Acknowledgment.—We are indebted to Herbert Ginsberg for assistance in the pharmacological testing of these compounds.

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

Unsaturated Macrocyclic Compounds. III.¹ Synthesis of Cyclohexadeca-1,3,9,11-tetrayne by a Novel Cyclization Reaction²

BY F. SONDHEIMER AND Y. AMIEL

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The terminal diacetylene octa-1,7-diyne (I) on oxidation with oxygen in the presence of cuprous chloride and ammonium chloride in aqueous ethanol has been found to give 8% of cyclohexadeca-1,3,9,11-tetrayne (VI) by a novel cyclization reaction. The major products of the reaction are hexadeca-1,7,9,15-tetrayne (II) and dotriaconta-1,7,9,15,17,23,25,31-octayne (IV). Under milder conditions essentially only the linear tetraacetylene II is formed.

The oxidative coupling of terminal acetylenes (R—C≡CH) to the corresponding α-diacetylenes (RC≡C—C≡CR), first discovered by Glaser nearly ninety years ago,³ is one of the few reactions in organic chemistry in which two molecules are linked together directly to give a symmetrical product. The reaction has become of considerable synthetic importance, since not only acetylenic hydrocarbons³ but also alcohols,^{4a,b} amines,^{4c} nitro compounds,^{4d} carboxylic acids^{4e,f} and esters^{4g} usually give the coupled products smoothly and in high yield. The reaction, which takes place under very mild conditions, may be brought about by oxidizing the cuprous derivative of the acetylene with air or oxygen,^{3,4a,b} cupric chloride,^{5a} hydrogen

peroxide,^{5b} potassium ferricyanide^{4d,e,5c} or simply by heating^{5d} and by oxidizing the Grignard derivative with iodine^{5e,f} or cupric halides.^{5e,g} Very recently Eglinton and Galbraith⁶ made the interesting discovery that the coupling can be brought about simply and under homogeneous conditions by treating the acetylene with excess cupric acetate in methanol and pyridine.

Although the aforementioned type of oxidative coupling of acetylenes has been studied extensively, when we started our investigation only compounds containing a single terminal acetylene had been submitted to it. It seemed to be of interest to investigate the reaction with terminal diacetylenes of type HC≡C—*n*—C≡CH. Firstly the normal coupled product (HC≡C—*n*—C≡C—C≡C—*n*—C≡CH), being again a terminal diacetylene, might react further to give an unsaturated linear long-chain compound of high molecular weight, or if isolated, could be a useful intermediate in synthetic

(1) (a) The paper by F. Sondheimer and Y. Amiel (THIS JOURNAL, **78**, 4178 (1956)) is to be considered Part I of this series; (b) for Part II see Y. Amiel, F. Sondheimer and R. Wolovsky (Proc. Chem. Soc., **22** (1957)).

(2) Presented before the Organic Chemistry Division at the 130th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1956.

(3) C. Glaser, *Ber.*, **2**, 422 (1869); *Ann.*, **154**, 159 (1870).

(4) *Inter al.* (a) K. Bowden, I. M. Heilbron, E. R. H. Jones and K. H. Sargent, *J. Chem. Soc.*, 1579 (1947); (b) J. B. Armitage, C. L. Cook, N. Entwistle, E. R. H. Jones and M. C. Whiting, *ibid.*, 1998 (1952); (c) J. D. Rose and B. C. L. Weedon, *ibid.*, 782 (1949); (d) A. Bayer, *Ber.*, **15**, 50 (1882); (e) **18**, 674, 2269 (1885); (f) H. K. Black and B. C. L. Weedon, *J. Chem. Soc.*, 1785 (1953); (g) T. Bruun, P. K. Christensen, C. M. Haug, J. Stene and N. A. Sørensen, *Acta Chem. Scand.*, **5**, 1244 (1951); **6**, 602 (1952); J. P. Riley, *J. Chem. Soc.*, 2193 (1953).

(5) *Inter al.* (a) F. Straus and L. Kollek, *Ber.*, **59**, 1664 (1926); (b) N. A. Milas and O. L. Mageli, THIS JOURNAL, **75**, 5970 (1953); (c) R. Lespiau, *Ann. chim.*, **11**, 281 (1897); **27**, 177 (1912); (d) J. S. Zalkind and F. B. Fundyler, *Ber.*, **69**, 128 (1936); (e) J. B. Armitage, E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.*, 2014 (1952); (f) H. K. Black, D. H. S. Horn and B. C. L. Weedon, *ibid.*, 1704 (1954); (g) J. P. Daney and J. A. Nieuwland, THIS JOURNAL, **58**, 1609 (1936); H. H. Schlubach and V. Franzen, *Ann.*, **572**, 116 (1951); L. Skattebøl and N. A. Sørensen, *Acta Chem. Scand.*, **7**, 1388 (1953).

(6) G. Eglinton and A. R. Galbraith, *Chemistry & Industry*, 737 (1956); see also F. Bohlmann and J. Politt, *Ber.*, **90**, 130 (1957).

work. Secondly the possibility existed that cyclic polyacetylenes might be formed by intramolecular coupling. In this paper we describe the results obtained by oxidizing the cuprous derivative of octa-1,7-diyne (I) with oxygen, a reaction which leads to both linear and cyclic polyacetylenes.⁷

Octa-1,7-diyne (I) was chosen for study since it may be obtained smoothly in high yield by condensation of the readily available 1,4-dibromobutane with sodium acetylide in liquid ammonia.⁸ It has been shown by Jones, Whiting, *et al.*,^{4b} that a convenient and mild method of performing the coupling reaction involves shaking the acetylene at room temperature with an aqueous acidified cuprous chloride-ammonium chloride mixture in air or oxygen. Octa-1,7-diyne (I) under these conditions gave essentially only one product, C₁₆H₁₈, m.p. 21°, in 57% yield (30% conversion). The infrared spectrum showed a band at 3300 cm.⁻¹ (acetylenic C-H stretching), indicative of the presence of a C≡CH grouping. In the C≡C stretching region the spectrum showed three separate maxima at 2235, 2135 and 2102 cm.⁻¹; the first two of these may be ascribed to a disubstituted α -diacetylene function and the third to the C≡CH grouping.⁹ No indications of the presence of an allene were found. The ultraviolet spectrum showed the three relatively low intensity maxima at 226, 238 and 253 m μ indicative of the α -diacetylene chromophore.^{4b} Catalytic hydrogenation yielded *n*-hexadecane (III), and the coupling product is therefore the normal dimer,¹⁰ hexadeca-1,7,9,15-tetrayne (II).

Under more vigorous conditions, involving the bubbling of air into a stirred mixture of the diacetylene in aqueous ethanol containing ammonium chloride, cuprous chloride and dilute hydrochloric acid at 55°,¹¹ octa-1,7-diyne (I) gave a mixture which was resolved into four entities (A, B, C and D in order of increasing polarity) by chromatography on alumina. Substance C, produced in highest yield (45%), proved to be the dimer II obtained previously. Next in yield (19%) was substance D, m.p. 92°, the spectral characteristics of which were rather similar to those of the normal dimer II. Its much lower solubility, higher melting point and the fact that it had a lower hydrogen content than II indicated the compound to be of higher molecular weight. Full hydrogenation led to *n*-dotriacontane (dicetyl) (V), and D must therefore be the tetramer, dotriacont-1,7,9,15,17,23,25,31-octayne (IV), formed by the further coupling

of the dimer II. Substance A, formed in *ca.* 5% yield by weight, contained chlorine; the infrared spectrum showed it not to be acetylenic, and its structure is still under investigation. The fourth substance B (8% yield) had a considerably higher melting point than II or IV and unlike these compounds gave no precipitate with silver nitrate in 95% ethanol. The absence of hydrogen bound to acetylene was confirmed by the infrared spectrum which showed bands at 2240 and 2154 cm.⁻¹ (disubstituted α -diacetylene)⁹ but none at *ca.* 3300 cm.⁻¹; compounds with a free ethynyl group all show a strong band at this position (acetylenic C-H stretching).⁹ Moreover the C≡CH stretching band at *ca.* 2100 cm.⁻¹ was absent (this is, however, a less reliable band on which to base conclusions since in a terminal acetylene (*e.g.*, II) it is much weaker than that at 3300 cm.⁻¹ and is relatively close to the other C≡C stretching bands). The elemental analysis indicated the formula (C₈H₈)_n, derived from I (C₈H₁₀) by the loss of the two acetylenic hydrogen atoms. All these facts suggested that substance B was cyclic, *viz.*, that an intramolecular coupling reaction had taken place.

The smallest ring containing an acetylenic bond capable of existence seems to be eight-membered.¹² Whereas a disubstituted acetylene consists of a rigid straight four-carbon chain, a disubstituted α -diacetylene consists of a straight six-carbon chain and the smallest ring containing this grouping would therefore be expected to be about twelve-membered. The direct cyclization of octa-1,7-diyne (I) to cycloocta-1,3-diyne is consequently ruled out, and it is of course quite impossible to construct a model of such a molecule. The cyclic dimer, cyclohexadeca-1,3,9,11-tetrayne (VI), in which the two parallel straight α -diacetylene chains are bound together on both sides by a tetramethylene bridge, is however quite unexceptional. Substance B was indeed shown to possess structure VI, since full hydrogenation yielded cyclohexadecane (VII) identical with an authentic specimen.¹³

In order to improve the yield of the cyclic dimer VI, the linear dimer II which was the main product was separately subjected to the coupling reaction. Hardly any reaction occurred under the conditions used for the preparation of II, IV and VI. However, when the ethanol:water ratio was increased to 9:1 (instead of the usual 2:8 ratio) and benzene was added so as to increase the solubility further, II gave a 31% yield of the linear tetramer IV and no trace of the cyclic dimer VI. It therefore appears that the latter must have been formed directly from two molecules of the monomer by coupling at both ends rather than *via* the dimer II which cyclizes internally.

(12) A. T. Blomquist and L. H. Liu, *THIS JOURNAL*, **75**, 2153 (1953).

(13) After completion of this part of our work, Eglinton and Galbraith kindly informed us that they had obtained a mixture of the cyclic monomers and cyclic dimers from terminal diacetylenes in which the acetylenes were separated by at least ten methylene groups, the cyclization being carried out by means of cupric acetate in methanol and pyridine under high dilution conditions (*cf.* footnote 6). At the time we were studying the coupling of tetradeca-1,13-diyne in the hope of obtaining the cyclic monomer; this work was abandoned and we decided to restrict our investigation to terminal diacetylenes in which the acetylene groupings were separated by a comparatively short chain.

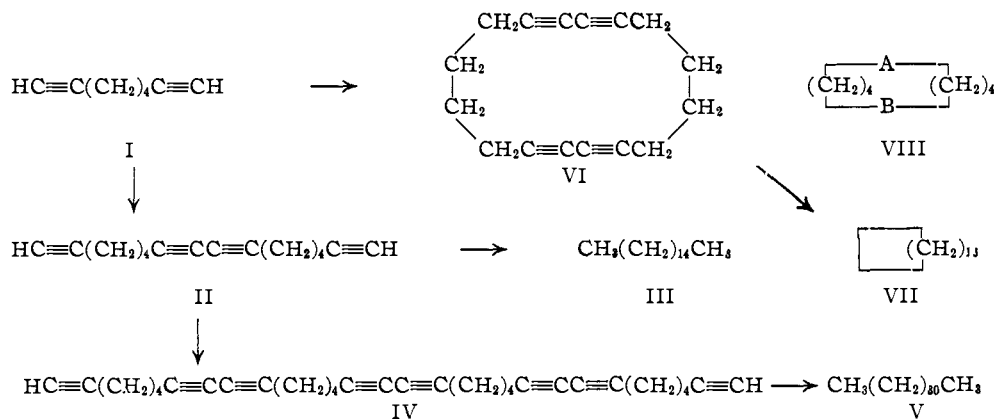
(7) For a preliminary communication, see footnote 1a.

(8) H. Bader, L. C. Cross, I. M. Heilbron and E. R. H. Jones, *J. Chem. Soc.*, 619 (1949).

(9) (a) *Cf.* N. Sheppard and D. M. Simpson, *Quart. Revs. (London)*, **6**, 1 (1952), Tables 2 and 3. All our spectra were measured in chloroform solution; under the same conditions the monosubstituted acetylene 1-hexyne showed ν_{\max} 3300 and 2102 cm.⁻¹, while the disubstituted α -diacetylene dodeca-5,7-diyne (the coupling product of 1-hexyne) showed ν_{\max} 2228 and 2142 cm.⁻¹.

(10) For convenience the terms "dimer" and "tetramer" are used to denote products derived, respectively, from two and four molecules of "monomer," although their empirical formulas are of course not exact multiples of the monomer.

(11) These conditions were found to result in the smooth coupling of secondary acetylenic carbinols (footnote 4a), which had been reported not to oxidize readily at room temperature (J. S. Zalkind, *et al.*, *Zhur. Obshchei Khim.*, **7**, 227 (1937); **9**, 971, 1725 (1939)).



Although single acetylenic linkages had previously been incorporated into carbocyclic rings,^{12,14} it was only after we had confirmed the structure of the cyclic tetraacetylene VI that other examples of carbocyclic poly-yne were reported.^{8,15} Cyclohexadeca-1,3,9,11-tetrayne (VI) is similar in structure to cyclododeca-1,7-diyne (VIII, A = B = $-\text{C}\equiv\text{C}-$),¹⁵ 5-[10]paracyclophane (VIII, A = $-\text{C}\equiv\text{C}-$, B = $-\text{C}_6\text{H}_4-$)¹⁶ and *p,p'*-tetramethylene-1,4-diphenylbutane (VIII, A = B = $-\text{C}_6\text{H}_4-$)¹⁷ studied by Cram and his co-workers. The ultraviolet spectrum of VI shows λ_{max} 227, 239 and 254 $\text{m}\mu$ (ϵ 580, 600 and 360, respectively; or 290, 300 and 180, respectively, per α -diacetylene group). Disubstituted α -diacetylenes are known to show λ_{max} ca. 227, 238 and 253 $\text{m}\mu$ (ϵ 300–400, 300–400 and 160–240, respectively).^{4b} The spectrum of VI is therefore normal and as in the case of the above-mentioned derivatives of VIII,^{15–18} the two unsaturated groups, which are separated by two tetramethylene bridges, are too far apart for appreciable electronic interaction to occur.

The generality of the novel cyclization reaction has been investigated, and the results are reported in a subsequent paper. The fact that the linear coupling stops at the tetramer stage is probably due to the low solubility of the C_{32} -hydrocarbon IV in the aqueous ethanol employed. Although the obtention of II and IV may be of use for synthetic purposes, it will be of interest to determine whether higher linear coupling products and perhaps improved yields of cyclic compounds can be obtained by carrying out this type of reaction in a homogeneous medium.

Acknowledgments.—We wish to express our thanks to Professor V. Prelog of the Eidgenössische Technische Hochschule, Zürich, for a sample of cyclohexadecane and to Professor H. H. Günthard

(14) M. Stoll, J. Hulstkamp and A. Rouvé, *Helv. Chim. Acta*, **31**, 543 (1948); V. Prelog, K. Schenker and H. H. Günthard, *ibid.*, **35**, 1598 (1952); A. T. Blomquist, R. E. Burge and A. C. Sucsy, *J. Org. Chem.*, **17**, 3636 (1952); A. T. Blomquist, L. H. Liu and J. C. Bohrer, *ibid.*, **18**, 3043 (1953).

(15) D. J. Cram and N. L. Allinger, *ibid.*, **78**, 2518 (1956). A heterocyclic diacetylene, containing two ether linkages in the ring, had been reported previously (R. Lespieau, *Compt. rend.*, **188**, 502 (1929)).

(16) D. J. Cram and M. Cordon, *THIS JOURNAL*, **77**, 4090 (1955).

(17) D. J. Cram and N. L. Allinger, *ibid.*, **76**, 726 (1954).

(18) D. J. Cram, N. L. Allinger and H. Steinberg, *ibid.*, **76**, 6132 (1954).

for the infrared identification of our cyclohexadecane at liquid air temperature.

Experimental¹⁹

Oxidation of Octa-1,7-diyne (I) at Room Temperature in Water.—A mixture of 24 g. of cuprous chloride and 38.4 g. of ammonium chloride in 100 cc. of water was adjusted to pH 3 by addition of concd. hydrochloric acid, and then 10 g. of octa-1,7-diyne (I)⁸ was added. The mixture was shaken with air in a Parr hydrogenation apparatus at room temperature for 6 hr.; water was then added and the product isolated with ether in the usual way. Direct distillation at 60 mm. furnished 4.8 g. of recovered starting material, and the residue was chromatographed on 250 g. of alumina. The fraction eluted with hexane yielded 2.95 g. (57% yield, 30% conversion) of hexadeca-1,7,9,15-tetrayne (II), m.p. 16–19°. A sample was purified by distillation (b.p. 119–120° (0.1 mm.)) and subsequent low temperature crystallization from pentane. It showed m.p. 21–22°, n_D^{20} 1.5205; λ_{max} 226, 238, and 253 $\text{m}\mu$ (ϵ , 525, 465 and 320, respectively); ν_{max} 3300 and 2100 cm^{-1} (terminal acetylene) and 2235 and 2135 cm^{-1} (disubstituted α -diacetylene). It gave an immediate heavy precipitate with a 5% solution of silver nitrate in 95% ethanol. The solid substance was photosensitive and after a few minutes in light it became coated with a blue film which gradually became pink.

Anal. Calcd. for $\text{C}_{16}\text{H}_{18}$: C, 91.37; H, 8.63. Found: C, 91.32; H, 8.80.

Further elution with hexane–benzene (1:1) produced 0.06 g. of the linear tetramer IV, m.p. 88–90°, further described below. Almost identical results were obtained when the oxidation was carried out in oxygen instead of air.

Oxidation of Octa-1,7-diyne (I) at 55° in Aqueous Ethanol.—A solution of 25 g. of octa-1,7-diyne in 50 cc. of ethanol was added to a mixture of 50 g. of cuprous chloride and 80 g. of ammonium chloride in 215 cc. of water containing 0.5 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 employed to prevent the diacetylene from being swept out of the reaction mixture. After 6 hr. at 55° (by which time a viscous insoluble gummy mass had separated), the product was isolated with benzene in the usual way. Starting material (1.2 g.) was recovered by distillation, and the residue (23.1 g.) was dissolved in 140 cc. of petroleum ether–benzene (1:1) (1.2 g. of polymeric material remained insoluble and was removed) and chromatographed on 1 kg. of alumina. Elution with petroleum ether–benzene (4:1) yielded successively 1.3 g. of a chlorine-containing non-acetylenic substance, 7.95 g. of a mixture of the cyclic dimer VI and the linear dimer II, which partially crystallized at 25°, and 5.04 g. of the almost pure linear

(19) Melting points and boiling points are uncorrected. All chromatograms were done with Alcoa activated alumina, grade F-20 (Aluminum Co. of America, Pittsburgh, Pa.). Infrared spectra were taken in chloroform solution with a Perkin–Elmer model 12C single beam spectrophotometer with sodium chloride prism. Ultraviolet spectra were determined in iso-octane 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.

dimer II (as judged by infrared comparison), m.p. 17–19°. Further elution with petroleum ether–benzene (1:1) yielded 4.66 g. (19%) of the tetramer IV, m.p. 82–86°.

Crystallization of the 7.95 g. of semi-solid mixture of II and VI from petroleum ether produced 1.65 g. (6.7%) of cyclohexadeca-1,3,9,11-tetrayne (VI) as hexagonal plates, m.p. 160–162° dec.; λ_{max} 227, 239 and 254 μ (ϵ 580, 600 and 360, respectively); ν_{max} 2240 and 2154 cm^{-1} (disubstituted α -diacetylene); no band at ca. 3300 cm^{-1} (absence of acetylenic hydrogen). The substance gave no precipitate with silver nitrate in 95% ethanol solution.

Anal. Calcd. for $\text{C}_{16}\text{H}_{16}$: C, 92.26; H, 7.74. Found: C, 92.48; H, 7.62.

The residue (6.3 g.) after removal of the crystalline VI completely solidified at 0° and showed m.p. 15–18°. Infrared analysis indicated the presence of over 90% of the linear dimer II. It was dissolved in 60 cc. of ethanol and was added to a solution of 12.5 g. of silver nitrate in 240 cc. of ethanol and 12.5 cc. of water. The immediate white precipitate was collected and washed well with ethanol. The filtrate was concentrated to small volume, diluted with water and well extracted with ether. The residue obtained by evaporation of the ether extract was crystallized from petroleum ether and yielded 0.32 g. of VI, m.p. 156–158°; the total yield was 1.97 g. or 8%. The pure linear dimer II could be regenerated from the silver salt by boiling with aqueous sodium cyanide solution.

The linear tetramer, dotriaconta-1,7,9,15,17,23,25,31-octayne (IV), eluted last from the column, was best purified by slow crystallization from a dilute methanol or ethanol solution. This method produced small plates, m.p. 93–94°; λ_{max} 226, 240 and 254 μ (ϵ 1190, 1140 and 720, respectively); ν_{max} 3305 and 2100 cm^{-1} (terminal acetylene) and 2235 and 2140 cm^{-1} (disubstituted α -diacetylene). The substance gave a white precipitate with silver nitrate in 95% ethanol solution.

Anal. Calcd. for $\text{C}_{32}\text{H}_{34}$: C, 91.81; H, 8.19. Found: C, 92.01; H, 7.98.

Oxidation of Hexadeca-1,7,9,15-tetrayne (II).—The oxidation of 1.7 g. of II together with 1.6 g. of cuprous chloride, 2.6 g. of ammonium chloride in 5 cc. of ethanol and 7 cc. of water at pH 3 was carried out at 55° by bubbling through

oxygen with stirring for 6 hr. Nearly all the starting material was recovered and only 0.017 g. (1%) of the linear tetramer IV, m.p. 90–92°, was obtained.

In another experiment the oxidation was performed by bubbling oxygen for 6 hr. through a stirred mixture of 5 g. of II, 5 g. of cuprous chloride and 8 g. of ammonium chloride in 180 cc. of ethanol, 20 cc. of water, 30 cc. of benzene and 0.05 cc. of concd. hydrochloric acid, at 55°. Isolation with benzene and chromatography on alumina gave 2.57 g. (51%) of recovered II and 1.56 g. (31%) of the linear tetramer IV, m.p. 91–93°.

***n*-Hexadecane (Cetane) (III).**—The linear dimer II (233 mg.) dissolved in 10 cc. of acetic acid was shaken in hydrogen over 40 mg. of platinum oxide at atmospheric pressure and room temperature until the uptake of gas ceased. The catalyst was removed, the solvent and then the product were distilled. The resulting *n*-hexadecane showed m.p. 17–18°, b.p. 276–278° (762 mm.), n_{D}^{20} 1.4355 (reported²⁰ m.p. 18°, b.p. 280° (760 mm.), n_{D}^{20} 1.4352).

***n*-Dotriacontane (Dicetyl) (V).**—The linear tetramer IV (100 mg.) was hydrogenated in a mixture of 5 cc. of dioxane and 20 cc. of acetic acid (due to its insolubility in the acid alone) over platinum oxide. The resulting *n*-dotriacontane after crystallization from ether showed m.p. 70°, undepressed on admixture with an authentic specimen (m.p. 70°).

Cyclohexadecane (VII).—The cyclic dimer VI (150 mg.) was hydrogenated in a mixture of 20 cc. of acetic acid and 5 cc. of hexane over 40 mg. of platinum oxide, as usual. The resulting cyclohexadecane after crystallization from methanol showed m.p. 60–61°, undepressed on admixture with an authentic specimen (m.p. 60–61°); reported²¹ m.p. 61°. Further proof of identity was provided by the fact that the infrared spectrum, measured in potassium bromide at liquid air temperature (when much fine structure appears), was completely identical with that of an authentic sample.

(20) 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.

(21) L. Ruzicka, W. Brugger, C. F. Seidel and H. Schinz, *Helv. Chim. Acta*, **11**, 496 (1928).

REHOVOTH, ISRAEL

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Reaction of α -Methylstyrene Catalyzed by Sodium¹

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The reaction of α -methylstyrene at its reflux temperature in the presence of sodium and sodium-benzylsodium catalyst was investigated. The products of the reaction were composed of cumene (V) 18% by wt., *p*-terphenyl (VI) 2.4%, 1-methyl-1,3-diphenylcyclopentane (VII) 32% and a trimer 19%. The structure of the dimer was established by means of synthesis and degradation. Compounds V and VI were products of a hydrogen transfer reaction. The effect of temperature upon the product distribution was investigated. The mechanism of the reaction was discussed and tested. The synthesis of VII was accomplished by the reaction of 1-methyl-3-phenylcyclopentene with benzene in the presence of hydrogen fluoride. The cycloalkylation reaction was accompanied by a hydrogen transfer reaction resulting in the formation of 1-methyl-3-phenylcyclopentane and 1-methyl-3-phenylcyclopentadiene.

The dimerization of α -methylstyrene in the presence of acid catalysts was reported to form compounds I, II and III, depending on the experimental condition and the nature of the catalyst used.^{4–6}

(1) Paper XI of the series Base Catalyzed Reactions of Hydrocarbons. For paper X, L. Schaap and H. Pines, *THIS JOURNAL*, **79**, 4967 (1957).

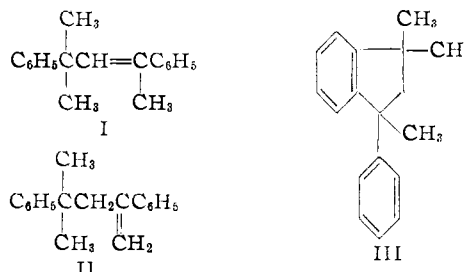
(2) Vladimir N. Ipatieff Postdoctoral Fellow 1955–1956.

(3) To whom requests for reprints should be addressed.

(4) For complete literature references see J. Hukki, *Acta Chem. Scand.*, **3**, 279 (1949).

(5) F. S. Dainton and R. H. Tomlinson, *J. Chem. Soc.*, 151 (1953).

(6) J. C. Petropoulos and J. J. Fisher, Division of Organic Chemistry American Chemical Society Meeting, Miami, Florida, April 12, 1957.



Bergmann and co-workers⁷ reported that α -

(7) E. Bergmann, H. Taubadel and H. Weiss, *Ber.*, **64**, 1493 (1931).