ether, and the ether combined with the ethyl acetate. After removing volatile solvents by distillation through a 10-cm. column, the product was distilled from a 2-ml. distillation unit provided with a short column. Water-white dodecane (0.54 g., $n^{25}\text{D}$ 1.4213) was collected after discarding a few drops of forerun. The thermometer in the vapors read 203–210°; the boiling point (micro) however was determined to be 219° (corrected). The boiling point and index of refraction of dodecane are recorded,[23] respectively, as 216.27° (760 mm.) and $n^{25}\text{D}$ 1.4195.

BOSTON, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF BOSTON UNIVERSITY]

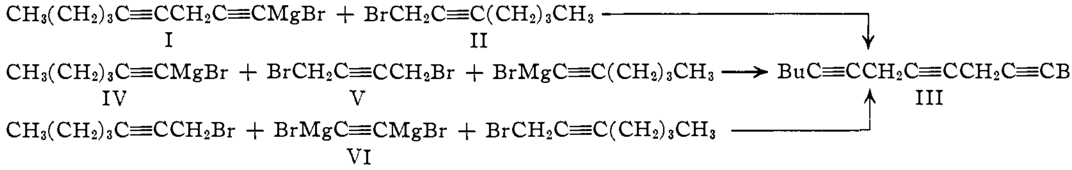
Hexadecatriyne-5,8,11

BY WALTER J. GENSLER AND A. P. MAHADEVAN

RECEIVED JUNE 22, 1955

Hexynylmagnesium bromide combines with 1,4-dibromobutyne-2 in the presence of cuprous chloride to give hexadecatriyne-5,8,11. The Grignard derivative of nonadiyne-1,4 combines with 1-bromoheptyne-2 to give the same product. Acetylenedimagnesium bromide with 1-bromoheptyne-2 fails to give hexadecatriyne-5,8,11.

The synthesis of hexadecatriyne-5,8,11 (III), a representative skipped triyne, has been investigated as part of a program on skipped unsaturation. Of the three methods tried two gave the desired product; the third did not. The cuprous chloride catalyzed coupling[1] of the Grignard derivative (I) of nonadiyne-1,4[2] with 1-bromoheptyne-2 (II)[3] did furnish hexadecatriyne-5,8,11 (III). The same material was obtained from the cuprous chloride catalyzed coupling of two moles of hexynyl Grignard reagent (IV) with 1,4-dibromobutyne-2 (V).[4,5] Reaction of two moles of 1-bromoheptyne-2 with one mole of acetylenedimagnesium bromide (VI), however, failed to yield hexadecatriyne-5,8,11.



$$\underset{\text{I}}{CH_3(CH_2)_3C{\equiv}CCH_2C{\equiv}CMgBr} + \underset{\text{II}}{BrCH_2C{\equiv}C(CH_2)_3CH_3}$$

$$\underset{\text{IV}}{CH_3(CH_2)_3C{\equiv}CMgBr} + \underset{\text{V}}{BrCH_2C{\equiv}CCH_2Br} + BrMgC{\equiv}C(CH_2)_3CH_3 \longrightarrow \underset{\text{III}}{BuC{\equiv}CCH_2C{\equiv}CCH_2C{\equiv}CBu}$$

$$CH_3(CH_2)_3C{\equiv}CCH_2Br + \underset{\text{VI}}{BrMgC{\equiv}CMgBr} + BrCH_2C{\equiv}C(CH_2)_3CH_3$$

The products from the two successful experiments were obtained as almost water-white liquids which, judging from the infrared (Fig. 1) and ultraviolet absorptions and the indices of refraction, were identical. The triyne was extremely sensitive to air, exposure developing color almost immediately. Continued exposure produced a dark brown firmly adhering resin.

Absence of branching was demonstrated by the formation of hexadecane on hydrogenation. The ultraviolet absorption curve for the coupling products had rounded, poorly defined, maxima at 220–228 mμ (ε approx. 450) and at 272 mμ (ε 480–580). However, neither the characteristic collection of maxima at 210–266 mμ shown by conjugated acetylenes[6] nor the high intensity absorption below 235 mμ shown by ene-ynes[6] was evident. Also, the observed molar refraction compared far less satisfactorily with the value calculated for a product with conjugated unsaturation than with the value for hexadecatriyne-5,8,11. Significant amounts of such groupings accordingly were precluded. Some indication of allenic linkages was obtained from infrared absorption in the 5.0–5.2 μ region. However the low intensity of this absorption as well as the low intensity of the ultraviolet absorption—assuming reasonably that allenic links in the coupling product would be conjugated to other unsaturation—sharply limited the amount of allenic impurities. The cluster of peaks around 4.5 μ was indicative of C≡C bonds (Fig. 1). The data, therefore, while pointing to some allenic impurity, are consistent with the skipped triyne formulation III for the bulk of the coupling product.

Acknowledgment.—The Office of Ordnance Research, U. S. Army, provided the funds that made this work possible (Research Project 751; Contract No. DA-19-020-ORD-1984). Thanks are also extended to the Indian Council of Medical Research for granting leave of absence to A.P.M. for the period of this investigation.

Experimental[7]

Hexadecatriyne-5,8,11 (III) from Nonadiyne-1,4 (I) and 1-Bromoheptyne-2 (II).—Ethylmagnesium bromide was prepared from 26.2 g. of ethyl bromide (0.24 mole) and 4.86 g. (0.20 g. atom) of shreds of sublimed magnesium,[8] with a total of 100 ml. of dry ether. The reaction mixture was stirred continuously, and was blanketed with dry nitrogen introduced at the top of the condenser through a calcium chloride tube. Nonadiyne-1,4 (28.1 g. or 0.234 mole), with $n^{25}\text{D}$ 1.4518, taken from a freshly opened ampoule was dissolved in 50 ml. of dry ether, and was added dropwise to the Grignard solution over a period of 1.5 hours. Evolution of gas and mild reflux were noted. One hour after

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[1] W. J. Gensler and A. P. Mahadevan, THIS JOURNAL, **77**, 3076 (1955).

[2] W. J. Gensler, A. P. Mahadevan and J. Casella, Jr., *ibid.*, **78**, 163 (1956).

[3] M. S. Newman and J. H. Wotiz, *ibid.*, **71**, 1292 (1949).

[4] G. Eglinton and M. C. Whiting, *J. Chem. Soc.*, 3650 (1950).

[5] Another example of the striking lack of any tendency of acetylenic Grignard reagents to combine with propargyl bromides was encountered with hexynylmagnesium bromide and 1,4-dibromobutyne-2. Little if any coupling occurred after a reaction period as long as 20 hours in boiling ether. Only after catalyst was added did the reaction proceed.

[6] See the papers cited in reference 1.

[7] Temperatures are uncorrected. Analyses were performed by Dr. Stephen M. Nagy and his assistants at Massachusetts Institute of Technology Microchemical Laboratory, and by Dr. Carol K. Fitz, 115 Lexington Avenue, Needham Heights 94, Massachusetts.

[8] We are indebted to Dow Chemical Co. for a generous sample of this magnesium.

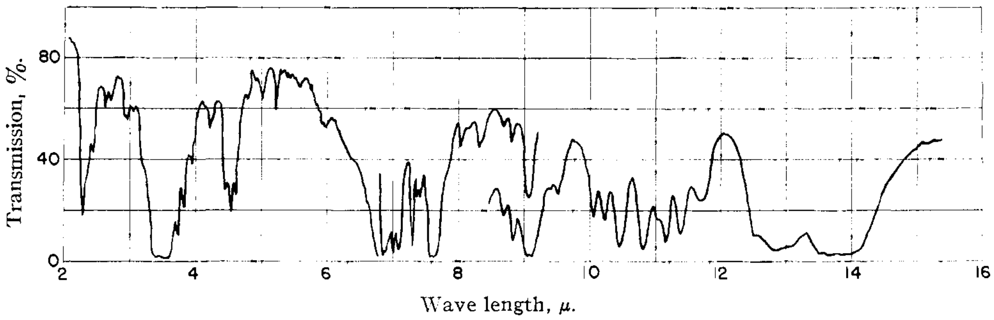

Fig. 1.—Infrared absorption spectrum of hexadecatriyne-5,8,11. The curve was taken with a 0.40-mm. layer of the product from hexyne-1 (IV) and 1,4-dibromobutyne-2 (V) using a Baird double beam spectrophotometer. The 7–9 μ region was covered with a solution of the triyne in carbon tetrachloride with carbon tetrachloride in the comparison cell. Neat liquid *vs.* an empty comparison cell was used for the other parts of the curve. The triyne from I and II gave a spectrum virtually superimposable on the one shown above.

addition of the nonadiyne-1,4, 0.5 g. of cuprous chloride was added to the dark amber mixture. Stirring for 15 minutes permitted the catalyst to dissolve. A solution of 28.0 g. (0.16 mole) of 1-bromoheptyne-2, $n^{25}\mathrm{D}$ 1.4882, in 50 ml. of dry ether was allowed to run in in approximately one-half hour. The level of the liquid was marked, and after an aliquot was removed for estimation of Grignard content,[1] the mixture was boiled for 70 hours. The original 0.170 mole of Grignard reagent in the 240 ml. of solution decreased to 0.068 mole after 50 hours and to 0.038 mole after 67 hours. No clear-cut separation into two layers occurred after 50 hours, nor was any yellow precipitate evident. The two layers and the yellow precipitate were noted after 70 hours.

The reaction mixture was hydrolyzed over 600 g. of crushed ice and 25 ml. of concentrated sulfuric acid. The ether layer was separated from the aqueous layer and from the yellow precipitate and, after two washes with 50-ml. portions of water, was dried over calcium chloride. Ether was removed from the filtered mixture by warming under water-pump vacuum. The dark amber residue was distilled first through a 5-cm. Vigreux column to get 8.55 g. of material boiling at 25–40° (1 mm.) and then through a Claisen head to get 24.9 g. of material with $n^{25}\mathrm{D}$ 1.4831 and b.p. 130–135° (0.1–0.6 mm.). A small intermediate fraction was rejected. The first fraction was largely nonadiyne-1,4, which as estimated from the bromine analysis (6.36% of Br) was contaminated with 1.19 g. of 1-bromoheptyne-2. This fraction was dissolved in approximately 20 ml. of 95% alcohol and was treated with 100 ml. of alkaline mercuric iodide solution (1.2 molar in mercuric iodide).[9] The precipitate was collected, washed with 30% alcohol, and crystallized once from 200 ml. of ethyl acetate. Glistening crystals, weighing 11.0 g. and melting 110.5–111°, of the mercury derivative of nonadiyne-1,4[2] were obtained.

The second fraction was taken as hexadecatriyne-5,8,11. The yield based on the 1-bromoheptyne-2 employed was 72%, and on the nonadiyne-1,4 employed was 50%. Recovery of nonadiyne-1,4 in the form of its mercury derivative was 68% of the amount used in excess over the 1-bromoheptyne-2.

The second fraction was redistilled under nitrogen through a 10-cm. column, and the almost water-white distillate sealed *in vacuo* in several ampoules. Material from newly opened ampoules was employed for analysis, for determination of the index of refraction ($n^{25}\mathrm{D}$ 1.4819), for the ultraviolet and infrared spectra, etc. Boiling points were noted at 102–105° (0.12 mm.) and at 100–103° (0.05–0.08 mm.). The density was determined at 25° as 0.8660.

Anal. Calcd. for $C_{16}H_{22}$: C, 89.7; H, 10.3. Found: C, 89.9; H, 10.5.

The mole refraction calculated for hexadecatriyne-5,8,11 from the bond values of Vogel[10] is 71.08. The Lorenz–Lorentz value is 70.57.

Hexadecatriyne-5,8,11 (III) from Hexynylmagnesium Bromide and 1,4-Dibromobutyne-2 (V).[4]—The di-*p*-toluenesulfonyl ester of 1,4-dihydroxybutyne-2[11] was prepared as described in the literature.[4] Anhydrous calcium bromide was formed by treating calcium carbonate with hydrobromic acid and heating the acid solution first in a porcelain dish over a free flame until most of the liquid was driven off and then in a muffle furnace at 600° for two hours. Ethanol (150 ml.) was distilled from calcium hydride directly onto 40 g. of anhydrous calcium bromide. Almost all of the calcium bromide dissolved to give a cloudy solution. A solution of 59.1 g. (0.15 mole) of the di-*p*-toluenesulfonic ester, m.p. 92–93°, in 150 ml. of dry chloroform was added rapidly. A clear solution developed, but after one hour of stirring cloudiness was evident again. The mixture was allowed to stand for 20 hours. Transformation of the mixture to a mass of white solids was noted after six hours. Water (400 ml.) was added, and the mixture was shaken thoroughly. The aqueous layer was separated and was extracted with two 150-ml. portions of petroleum ether (b.p. 35–37°). The combined chloroform and petroleum ether solutions were washed with two portions of water and were dried over anhydrous calcium bromide. After removal of drying agent and of solvents, the crude product was distilled through a 10-cm. column to get 28.5 g. (90%) of water-white 1,4-dibromobutyne-2 boiling at 54–59° (approximately 1.2 mm.) and showing $n^{25}\mathrm{D}$ 1.5847. The value observed before was $n^{20}\mathrm{D}$ 1.5877.[4]

A solution of 27.1 g. (0.33 mole) of hexyne-1 in 50 ml. of dry ether was added to ethylmagnesium bromide prepared from 36.0 g. (0.33 mole) of ethyl bromide, 6.29 g. (0.26 g. atom) of shredded sublimed magnesium, and 200 ml. of ether. The mixture was boiled for one to two hours. 1,4-Dibromobutyne-2 (28.5 g. or 0.135 mole) in 50 ml. of dry ether was added in the course of about 15 minutes, and the mixture was then stirred and boiled for 20 hours. Comparison of aliquots taken from this mixture at the beginning and at the end of this period showed that very little Grignard reagent had been consumed, the Grignard content at the beginning being 0.257 mole and at the end 0.249 mole. Cuprous chloride (0.75 g.) was added, and the mixture, which was somewhat cloudy, was boiled and stirred for 72 hours. Twenty-four hours after addition of the cuprous chloride the Grignard content was 0.168 mole, and a very small lower layer was seen. Forty-eight hours after addition of the cuprous chloride aliquots taken from both layers showed that only 0.048 mole of Grignard remained. A solid more white than yellow was noted. Seventy-two hours after addition of the cuprous chloride the liquid layers were almost equal in volume, and aliquots taken from both layers showed that 0.014 mole of Grignard still remained. The precipitate at this point was distinctly yellow.

The reaction mixture was quenched over crushed ice and concentrated sulfuric acid, the ether layer was separated, washed with three 50-ml. portions of water, filtered to remove the yellow solid, and dried over calcium chloride. The drying agent and the solvent were removed, and the crude product distilled in a Claisen flask. A forerun (3.68 g.), probably unreacted 1,4-dibromobutyne-2, was collected

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[9] See J. R. Johnson and W. L. McEwen, This Journal, **48**, 469 (1926).

[10] A. Vogel, *et al.*, *J. Chem. Soc.*, 514 (1952).

[11] Very kindly furnished by General Aniline and Film Corp.

with b.p. 44–110° (0.3 mm.). Hexadecatriyne-5,8,11 (18.5 g., or 64% yield based on 1,4-dibromobutyne-2 used) was taken at 110–120° (mostly at 119–120°) (0.3 mm.). Redistillation permitted recovery of almost all of this hexadecatriyne-5,8,11 (b.p.'s 100–101° (0.1 mm.) and 114–115° (0.2–0.25 mm.)), which was collected and sealed without breaking the vacuum in several ampoules. The index of refraction was $n^{25}\mathrm{D}$ 1.4818.

Anal. Calcd. for $C_{16}H_{22}$: C, 89.7; H, 10.3. Found: C, 89.46; H, 10.39.

Ultraviolet Absorption.—Ultraviolet absorption curves were determined using 10^{-3} *M* solutions of hexadecatriyne-5,8,11 in 95% alcohol. The product from nonadiyne-1,4 and 1-bromoheptyne-2 had λ_{max} 273 mμ (ε 480); the product from hexyne-1 and 1,4-dibromobutyne-2 has λ_{max} 272 mμ (ε 580). Both products had poorly defined maxima in the 220–228 mμ region (ε *ca.* 450). Actually, because of the presence of impurities, we are in no position to claim that the observed maxima are characteristic features of the skipped triyne system.

Hexadecane from Hexadecatriyne-5,8,11.—A sample of hexadecatriyne-5,8,11 (2.8356 g. or 0.01323 mole) prepared from nonadiyne-1,4 and 1-bromoheptyne-2 was transferred from a freshly opened ampoule to a flask containing 30 ml. of ethyl acetate (J. T. Baker analyzed reagent), and was hydrogenated at room temperature in the presence of 100 mg. of platinum oxide catalyst. Absorption of hydrogen ceased after ten hours at which time 94% of the theoretical six moles of hydrogen had been taken up. The mixture was filtered, and the catalyst rinsed on the funnel with 20 ml. of ethyl acetate. Solvent was removed from the filtrate with the help of a current of air at temperatures no higher than 100°. The dark amber residue was distilled in a Claisen flask to furnish 2.33 g. (78%) of water-white hexadecane, b.p. 105–105.5° (1 mm.) and $n^{22.5}\mathrm{D}$ 1.4336. A few drops of forerun were rejected. The "Dreisbach–Dow Chemical Company Compilation of Physical Constants" gives b.p. 104.89° (1 mm.) for hexadecane; Egloff records $n^{22.5}\mathrm{D}$ 1.4335.[12]

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[12] G. Egloff, "Physical Constants of Hydrocarbons," Vol. V (Revised Values), American Chemical Society Monograph No. 78, Reinhold Publishing Corp., New York, N. Y., 1953.

BOSTON, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BOSTON UNIVERSITY]

Configuration of 9,10-Dihydroxystearic Acid[1]

BY WALTER J. GENSLER AND HERBERT N. SCHLEIN

RECEIVED JULY 15, 1955

9,10-Dihydroxyoctadecanedioic acid, m.p. 121–122°, is shown to be the racemic form by resolution with brucine. The half-ester of this acid is reduced with sodium and alcohol to 9,10,18-trihydroxystearic acid. This acid is tosylated, the 18-tosyloxy derivative is converted to the 18-iodo compound, and the iodo group is removed with zinc to give *threo*-9,10-dihydroxystearic acid, m.p. 94.5–95°.

Various methods have been employed in assigning the *erythro* configuration to "high melting" 9,10-dihydroxystearic acid (m.p. 131–132°) and the *threo* configuration to "low-melting" 9,10-dihydroxystearic acid (m.p. 94–95°).[2] Yet among the methods reported, the most reliable of all, that is, relating the *erythro* form to a demonstrably *meso* derivative, or the *threo* form to a demonstrably *racemic* derivative, is not to be found. Böeseken and Belinfante[3] did attempt something on this order by relating the 9,10-dihydroxystearic acids to the 9,10-dihydroxyoctadecanes. However, difficulty with the resolution of racemic 9,10-dihydroxyoctadecane blocked completion of their plans. In the work described in the present paper, we have established the configuration of the 9,10-dihydroxyoctadecanedioic acids (I), and have converted the racemic form by steps not involving the groups at 9 and 10 to 9,10-dihydroxystearic acid, m.p. 94.5–95°. These relations provide independent and definitive proof that "low melting" 9,10-dihydroxystearic acid has the *threo* configuration.

Resolution of 9,10-dihydroxyoctadecanedioic acid (I) (phloionic acid), m.p. 121–122°,[4,5] with strychnine or with quinine failed. A crystalline brucine salt of acid I formed smoothly, but the usual fractional crystallization gave no sign of resolution. However when the brucine salt was repeatedly leached with alcohol, and the acid was recovered from the undissolved salt, a distinct rotation was observed. Optical activity persisted in the benzoyl derivative of the regenerated acid. The fact that the 121–122° acid I could be obtained with optical activity clearly establishes this form as the racemic modification.[6]

An attempt was made to apply an attractive alternate scheme—noteworthy in that resolution is not involved—in determining the configuration of the two 9,10-dihydroxyoctadecanedioic acids. The benzylidene derivative of the racemic dihydroxy diacid can exist in only *one* form, and was in fact obtained as a single material. *A priori*, the benzylidene derivative of the *meso*-dihydroxy diacid can exist in *two* forms, both *meso*. It follows that the dihydroxy diacid leading to *one* benzylidene derivative is the *dl*-form, and that the dihydroxy diacid leading to *two* derivatives is the *meso* form. Disappointingly, the latter two benzylidene derivatives were not obtained pure, so that the scheme, realized only in part, did not furnish clear-cut conclusions. In principle, the method is related to the work of Wislicenus[7] on the configuration of the two 2,5-dimethylcyclopentane-1,1-dicarboxylic acids.

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[1] Abstracted from the dissertation submitted by Herbert N. Schlein in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Boston University Graduate School.

[2] For pertinent work and for leading references see D. Swern, L. P. Witnauer and H. B. Knight, THIS JOURNAL, **74**, 1655 (1952). Also *cf.* T. P. Hilditch "The Chemical Constitution of Natural Fats," Second Edition (revised), Chapman and Hall, Ltd., London, 1947.

[3] J. Böeseken and A. H. Belinfante, *Rec. trav. chim.*, **45**, 914 (1926).

[4] *Cf.* W. J. Gensler and H. N. Schlein, THIS JOURNAL, **77**, 4846 (1955).

[5] In the course of the present work, we have found that phloionic acid I, isolated from cork,[4] has no observable optical activity.

[6] Note ref. 4 as well as L. Ruzicka, Pl. A. Plattner and W. Widmer, *Helv. Chim. Acta*, **25**, 1086 (1942); H. Hunsdiecker, *Ber.*, **77**, 185 (1944); I. Ribas and E. Seoane, *Anales Real soc. españ. fis. y quim.* (series B), 963 (1954); G. Dupont, R. Dulou and J. Cohen, *Compt. rend.*, **240**, 875 (1955).

[7] J. Wislicenus, *Ber.*, **34**, 2565 (1901).