

of dilute sodium hydroxide solution. After treating with carbon the solution was filtered and acidified with acetic acid. The crystalline precipitate was collected and air-dried; yield 13 g. (90%). An analytical sample was recrystallized from water, darkened but unmelted at 360°.

Anal. Calcd. for $C_8H_8N_4O_2$: C, 43.37; H, 3.64; N, 33.73. Found: C, 43.57; H, 3.87; N, 33.98, 33.55.

The same compound was obtained in 50% yield by treating diethyl 1-formyl-2-diethoxymethylsuccinate¹⁸ in ethanol with excess hydrazine. It was identified by infrared spectrum.

3,3'-Dihydroxy-5-methyl-4,4'-bis-pyrazole (XVIIb).—This was obtained in 90% yield by heating 10 g. of 1-methyl-4,7-dihydroxy-2-oxa-5,6-diazaindene (XI) with 20 ml. of hydrazine hydrate on the steam-bath for eight hours.

A sample for analysis was sublimed at 275° under 0.1 mm. pressure; m.p. above 360°.

Anal. Calcd. for $C_7H_8N_4O_2$: C, 46.66; H, 4.48; N, 31.10. Found: C, 46.66; H, 4.76; N, 31.11.

In the same way 3,3'-dihydroxy-5,5'-dimethyl-4,4'-bis-pyrazole (XVIIc) was prepared in 52% yield by heating 1,3-dimethyl-4,7-dihydroxy-2-oxa-5,6-diazaindene (XV) with hydrazine under reflux for 15 hours; m.p. above 375°.

Anal. Calcd. for $C_9H_{10}N_4O_2$: C, 49.48; H, 5.19; N, 28.85. Found: C, 49.55; H, 5.32; N, 28.88.

A sample prepared by the method of Curtius⁹ had an infrared spectrum identical with that of the product described above.

INDIANAPOLIS, INDIANA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF BOSTON UNIVERSITY]

Preparation and Constitution of Nonadiyne-1,4

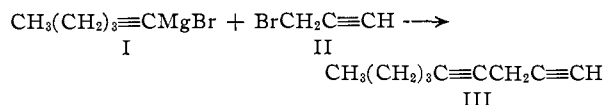
BY WALTER J. GENSLER, A. P. MAHADEVAN AND JOSEPH CASELLA, JR.

RECEIVED FEBRUARY 4, 1955

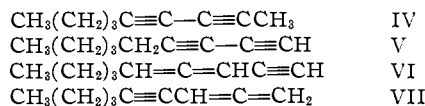
Hexynylmagnesium bromide and propargyl bromide in the presence of cuprous chloride couple to give the terminally unsaturated skipped diyne, nonadiyne-1,4. Available evidence shows that although an allenic impurity is present, the bulk of the coupling product has the assigned structure. Some features of terminally deuterated nonadiyne-1,4 are discussed. Dodecatriyne-1,4,7 is obtained as a minor product in the coupling reaction.

Acetylenic Grignard reagents in the presence of cuprous chloride couple with propargyl bromides to form skipped diynes.¹ In this way, for example, hexynylmagnesium bromide and 1-bromoheptyne-2 give tridecadiyne-5,8,¹ and heptynylmagnesium bromide and 1-bromoöctyne-2 give pentadecadiyne-6,9.² The subject of the present paper is nonadiyne-1,4 (III), a compound selected for study as a representative terminally unsaturated skipped diyne, and also for use in further synthetic work.

Coupling of hexynylmagnesium bromide (I) and



propargyl bromide (II), although slower than the coupling of hexynylmagnesium bromide and 1-bromoheptyne-2, proceeded without difficulty to form nonadiyne-1,4 (III). The material, a water-white liquid, became yellow on standing sealed and darkened rapidly on exposure to air. The coupling product was expected to have structure III; but just as with other products from propargyl bromides, the possibility of rearrangement during or after coupling³ made it necessary to consider isomeric structures—for example, conjugated diynes IV and V or allene acetylenes VI and VII.



First, however, an estimate of homogeneity was sought.

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

(2) W. J. Gensler and G. R. Thomas, *ibid.*, **73**, 4601 (1951).

(3) See the discussion in reference 1. Also note L. Piaux and M. Gaudemar, *Compt. rend.*, **240**, 2328 (1955).

Treatment of the coupling product with mercuric iodide dissolved in aqueous alcoholic sodium hydroxide solution⁴ precipitated a crystalline mercury derivative, m.p. 109–111°, in over 90% yield. To determine whether the unmodified coupling product or *isomerized* material was the immediate precursor of the derivative, the coupling product was exposed briefly to the alkaline solution before adding mercuric iodide. The same solid was obtained, but the yield dropped sharply. Clearly, alkali under the conditions of the formation of the mercury derivative was able to modify the coupling product. But fortunately the change, whatever its nature, operated to *decrease* the yield of derivative so that the observed yields were minimal measures of the content of original hydrocarbon. These experiments showed accordingly that a single substance comprised *over 90%* of the coupling product.

Formation of nonane on addition of four moles of hydrogen to the coupling product confirmed the absence of branching. Because ozonolysis yielded valeric acid, the unsaturation was confined to the first five carbons of the chain. Furthermore the absence of any sign of caproic acid rendered structure V highly improbable. Formation of silver and copper derivatives in addition to the above-mentioned mercury derivative established the presence of a terminal acetylene grouping, and thereby eliminated the possibility of structures IV and VII.

Considerations based on molar refraction and on ultraviolet absorption favored structure III over VI or VII. The Lorenz-Lorentz value (39.95) agreed closely with the molar refraction calculated for the skipped diyne III (39.97) but was 2.26 units lower than the value expected for the allenic acetylenic structures. The observed ultraviolet

(4) J. R. Johnson and W. L. McEwen, *THIS JOURNAL*, **48**, 469 (1926).

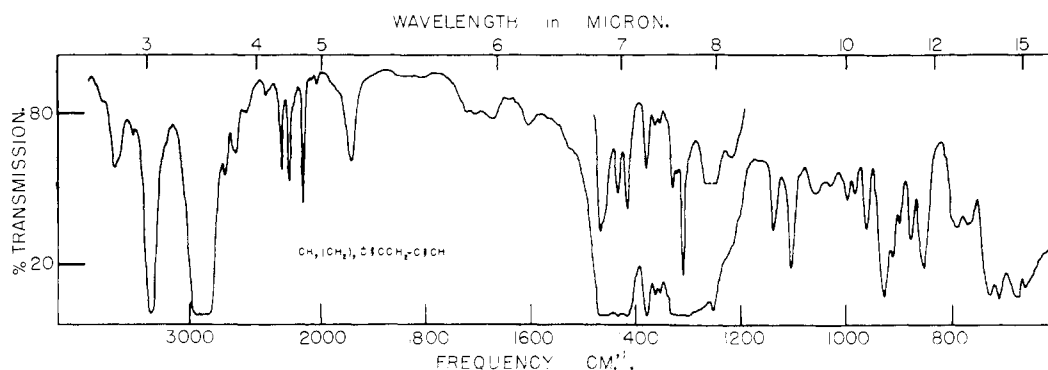


Fig. 1.—Infrared absorption for nonadiyne-1,4 taken with a 0.15 mm. layer of neat liquid in a Perkin-Elmer (model 21) spectrophotometer.⁸ The upper curve in the 1200–1500 cm^{-1} region was obtained with a solution of 0.45 ml. of nonadiyne-1,4 diluted with 1 ml. of carbon tetrachloride.

maximum at $214 \text{ m}\mu$ (ϵ 631)⁵ was not consistent with the intense absorption⁶ expected of the conjugated vinylacetylene systems⁷ in VI or VII. The infrared absorption curve⁸ (Fig. 1) confirmed the presence of acetylenic hydrogen by showing the characteristic peak at 3.03μ (3300 cm^{-1}). Also present were three well-defined peaks clustered in the wave length region associated with the $\text{C}\equiv\text{C}$ stretching vibration, that is, at 4.35μ (2300 cm^{-1}), 4.46μ (2240 cm^{-1}) and 4.69μ (2135 cm^{-1}).⁹ A definite peak was apparent also at 5.15μ (1942 cm^{-1}). Since absorption at this point is commonly considered to be diagnostic of the allenic linkage,^{10–12} here was a datum inconsistent with diyne structure III.

The 5.15μ Absorption in Nonadiyne-1,4.—One explanation for this allenic absorption where apparently there is no allenic grouping was that enough allenic material (*e.g.*, VI or VII) was present as impurity to give a detectable infrared absorption peak, but not enough to show up in the ultraviolet or in the molar refraction. Another entirely different interpretation was also considered, *viz.*, that the 5.15μ peak corresponded to the second overtone of an angle deformation vibration of the acetylenic C–H bond, the fundamental of which falls in the $600\text{--}700 \text{ cm}^{-1}$ region.¹³ Removing all impurities from the nonadiyne-1,4 would help in

(5) Actually even this low intensity absorption may be not so much a property of nonadiyne-1,4 as of the isomeric impurities present in small amounts.

(6) $\log \epsilon$ greater than 4 in the range $200\text{--}235 \text{ m}\mu$; see footnotes 20 and 22 of reference 1.

(7) *Cf.* W. D. Celmer and I. A. Solomons, *THIS JOURNAL*, **75**, 1372 (1953).

(8) We are indebted to Mrs. Erika Smakula of Boston University Medical School for placing the Perkin-Elmer (model 21) spectrophotometer in her department at our disposal, and for her assistance.

(9) Three triple bond absorption peaks for a compound that could have no more than two triple bonds were encountered before in the spectrum for tridecadiyne.^{3,8}

(10) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954.

(11) N. Sheppard and D. M. Simpson, *Quart. Revs.*, **6**, 1 (1952).

(12) J. H. Wotiz and W. D. Celmer, *THIS JOURNAL*, **74**, 1860 (1952).

(13) *Cf.* Bellamy¹⁰ and also Sheppard and Simpson.¹¹ Actually Fig. 1 does show maxima that could correspond to the fundamental (*e.g.*, 662 or 675 cm^{-1}), to the first overtone (1310 cm^{-1}), and to the second overtone (the 5.15μ or 1942 cm^{-1} peak). The absence of smooth variation in the spacing of the maxima did not preclude their relation as a fundamental and overtones.¹⁴

(14) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 264; also *cf.* W. Kaye, *Spectrochimica Acta*, **6**, 257 (1954).

deciding between the two explanations. With this in mind regeneration of pure hydrocarbon from the sharp-melting mercury derivative¹⁵ was attempted. The process, however, proved more difficult than anticipated and pure regenerated nonadiyne-1,4 did not become available for examination. If an analogous terminally unsaturated *solid* skipped diyne could be obtained and recrystallized to constant melting point, it could serve just as well in the same way as pure nonadiyne-1,4. However the attempted preparation of tricosadiyne-1,4, which was expected to be solid at room temperature, did not succeed.

A third and successful test involved replacing the acetylenic hydrogen in nonadiyne-1,4 with deuterium. If the 5.15μ peak were attributable to allenic impurities, the peak should not shift on deuteration, but if the peak were attributable to an acetylenic hydrogen vibration it should shift considerably to higher wave lengths. Infrared comparisons were made with nonadiyne-1,4 regenerated from nonadiynylmagnesium bromide by reaction on the one hand with ordinary water and on the other with deuterium oxide. Figure 2 shows that when the acetylenic hydrogen has been largely replaced with deuterium (that is, when the acetylenic C–H absorption at 3.03μ has largely disappeared in favor of the new acetylenic C–D absorption at 3.88μ), the 5.15μ absorption does not shift. Therefore the overtone hypothesis is unacceptable, and we must attribute the 5.15μ peak in the nonadiyne-1,4 to small amounts (0–7%) of allenic impurities.

A new absorption band in the deuterated material at 5.02μ (*cf.* Fig. 2) calls for comment. Assignment of an aliphatic C–D¹⁶ stretching vibration to this band is unlikely since such vibrations generally come no higher than 4.86μ .¹⁷ Instead we suggest that the new 5.02μ peak corresponds to

(15) The mercury derivative pressed in a potassium bromide pellet showed no sign of absorption at 5.15μ .⁸

(16) The deuteration procedure did not exclude formation of such bonds. Hydrogen on a skipped position can be metalated with ethylmagnesium bromide [Tchao Yin Lai, *Bull. soc. chim.*, [4] **53**, 1537 (1933); V. Grignard and L. Lapayre, *Compt. rend.*, **192**, 250 (1931)], and therefore appearance of deuterium on the 3 as well as on the 1, position cannot be disregarded. It is anticipated that study of the active hydrogens in this and other skipped diynes will be aided by following the deuteration quantitatively.

(17) H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangle, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 43.

the stretching vibration of the terminal $C\equiv C$ bond, and that its counterpart in the original nonadiyne-1,4 is the $4.69\ \mu$ peak. Exchange of terminal H by D not only shifts the acetylenic C-H vibration (from 3.03 to $3.88\ \mu$) but also shifts the terminal $C\equiv C$ stretching vibration (from 4.69 to $5.02\ \mu$).¹⁸

Dodecatriyne-1,4,7.—After removing nonadiyne-1,4 from the crude coupling product, dodecatriyne-1,4,7 was obtained in 10% yield as a high-boiling fraction. This skipped triyne, which distilled as a water-white liquid, acquired color almost instantaneously on exposure to air. Hydrogenation yielded dodecane. Infrared absorption at $3.09\ \mu$ as well as precipitation with alkaline mercuric iodide showed the presence of acetylenic hydrogen. A peak at $5.15\ \mu$ indicated the presence of allenic impurities.

Acknowledgment.—We take this opportunity to acknowledge the financial support of Office of Ordnance Research, U. S. Army (Research Project 751; Contract No. DA-19-020-ORD-1984). Thanks are extended also to the Indian Council of Medical Research for granting leave of absence to A.P.M., and to Professor R. C. Lord of Massachusetts Institute of Technology for his help and advice.

Experimental¹⁹

Nonadiyne-1,4 (III) from Hexynylmagnesium Bromide and Propargyl Bromide.—A solution of hexynylmagnesium bromide was prepared as described before¹ from 16.0 g. (0.66 g. atom) of magnesium covered with 250 ml. of dry ether, 87.2 g. (0.80 mole) of ethyl bromide in 100 ml. of dry ether and 65.6 g. (0.80 mole) of hexyne-1 in 100 ml. of dry ether. The solution was kept under dry nitrogen and was stirred throughout the reaction. To the hexynyl Grignard was added 2.0 g. (0.02 mole) of cuprous chloride. Then, over a period of 12 hours, 63.0 g. (0.53 mole) of propargyl bromide²⁰ was added to the gently boiling mixture. The mixture was boiled and stirred further for 48 hours. By this time two well-defined layers were evident, and approximately 80–90% of the Grignard reagent had reacted. Isolation of product in the usual manner¹ furnished 35.1 g. (56% based on propargyl bromide) of faintly yellow nonadiyne-1,4, with b.p. 85 – 88° ($47\ \text{mm.}$). Two fractionations in a one-piece glass still fitted with a 10-cm. Vigreux column afforded very faintly yellow product, which was collected in a number of tubes and sealed *in vacuo*. The loss on redistillation was 7%. Properties observed for nonadiyne-1,4 are as follows: b.p. 83 – 84° ($41\ \text{mm.}$), n_D^{25} 1.4518, density (25°) 0.81117; molar refraction, calcd. for nonadiyne-1,4 (III), 39.97²¹; calcd. for allenic compounds VI or VII, 42.21²¹; found from the Lorenz-Lorentz relation, 39.95.

(18) We have observed the same effect in the simpler compound, hexyne-1. The $C\equiv C$ vibration at $4.72\ \mu$ decreases in intensity in (partially) deuterated hexyne-1, and at the same time a new band appears at $5.03\ \mu$. The decrease in the $C\equiv C$ stretching frequency for acetylene, monodeuteroacetylene and dideuteroacetylene, which has been analyzed by Herzberg (ref. 14, p. 289), is another example of this effect.

(19) 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.

(20) Boiling point 81 – 82° , n_D^{25} 1.4897. This material was distilled from a sample of propargyl bromide very kindly provided by General Aniline and Film Corporation.

(21) The values are obtained from the bond refractions given by A. I. Vogel, *et al.* [*J. Chem. Soc.*, 514 (1952)]. To the value (40.77) calculated for VI or VII considering the system to contain two isolated double bonds and one isolated triple bond was added 0.44—the exaltation found for allenes [T. L. Jacobs and W. F. Brill, *THIS JOURNAL*, **75**, 1314 (1953)]—and 1.0—the exaltation associated with a conjugated ene-yne [J. Cymerman-Craig, E. G. Davis and J. S. Lake, *J. Chem. Soc.*, 1874 (1954)].

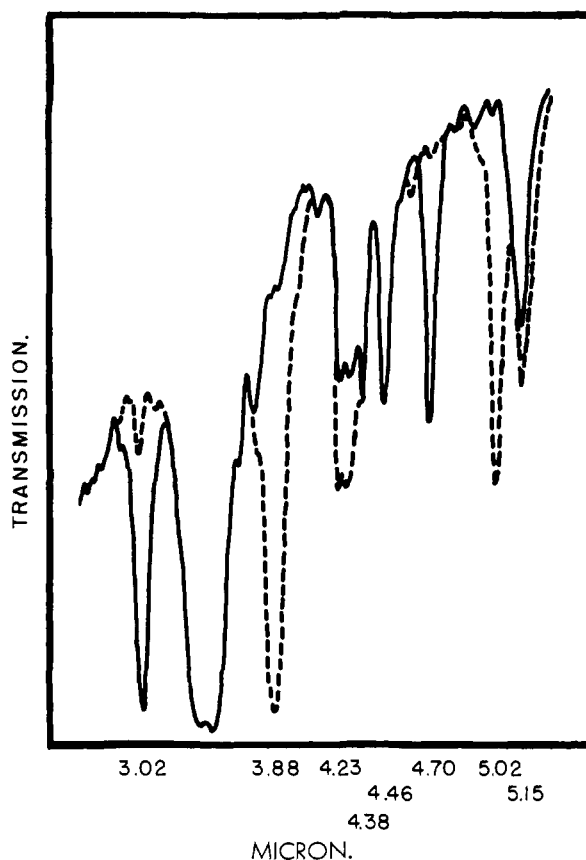


Fig. 2.—Comparison of infrared absorptions for terminally deuterated nonadiyne-1,4 and for nonadiyne-1,4 (see Experimental). Where absorptions are different, the dashed line refers to the deuterated material. The curves were taken using a 0.15 mm. layer of neat liquid in a Perkin-Elmer single-beam (model 12C) spectrophotometer. Note that the $4.35\ \mu$ absorption is overlapped in part by the twin atmospheric CO_2 bands at 4.23 and $4.28\ \mu$. The slightly greater intensity of the $5.15\ \mu$ peak of the deuterated material is attributable to an increase in the amount of allenic impurities developing during the deuteration process. The small differences in the positions of the absorption at 3.02 and at $4.70\ \mu$ when compared to the corresponding absorptions in Fig. 1 are not considered significant.

Anal. Calcd. for C_9H_{12} : C, 89.93; H, 10.06. Found (for a sample with n_D^{25} 1.4520 and b.p. 83° (approximately 36 mm.)): C, 90.1; H, 9.8.

The coupling product gave a white precipitate with alcoholic silver nitrate and a yellow precipitate with ammoniacal cuprous chloride.

A 10^{-8} molar solution of nonadiyne-1,4 in alcohol showed a rounded absorption maximum at $214\ m\mu$ (ϵ 631).

Attempted Preparation of Tricosadiyne-1,4.—Eicosyne-1 (n_D^{25} 1.4414, m.p. 34 – 35°) was obtained in 56% yield from octadecyl bromide and sodium acetylide.²² A solution of 2.25 g. of eicosyne-1 (0.0080 mole) in 75 ml. of ether was refluxed and stirred for 2.5 hours with ethereal ethylmagnesium bromide prepared from 0.19 g. of magnesium (0.0080 g. atom) and 0.94 g. of ethyl bromide (0.0085 mole). Cuprous chloride (0.03 g.) was added, and the mixture was boiled further for 15 minutes before adding 0.89 g. of propargyl bromide (0.0075 mole). The mixture, brought to a volume of 200 ml. by addition of dry ether, was boiled for 66 hours. Pure nitrogen blanketed the Grignard solutions at all times. Titration showed no consumption of Grignard

(22) O. R. Sammul, C. A. Hollingsworth and J. H. Wotiz, *THIS JOURNAL*, **75**, 4856 (1953).

reagent. After treating the reaction mixture in the usual way, 1.47 g. of unchanged eicosyne-1 was recovered, and no sign of tricosadiyne-1,4 was observed.

The reluctance to couple here is tentatively attributed to a molecular weight effect. The point will be investigated.

Mercury Derivative of Nonadiyne-1,4.—(A) Nonadiyne-1,4 (4.0 g.) dissolved in 25 ml. of 95% alcohol was added dropwise during a 3 to 4-minute interval to 60 ml. of an alkaline mercuric iodide solution (*ca.* 1.4 molar) made up according to Johnson and McEwen.⁴ The reaction mixture was stirred vigorously during, and for three minutes after, the addition of nonadiyne-1,4. The precipitate was removed by filtration, washed three times with 30% alcohol and once with petroleum ether. After drying in a vacuum desiccator overnight the crystalline almost pure white product weighed 6.8 g. (93%) and melted at 109–111°. A sample of the mercury derivative was crystallized from benzene-petroleum ether (b.p. 30–65°). The colorless needles, m.p. 111°, were dried at 50° *in vacuo* for two hours before analysis.

Anal. Calcd. for $(C_8H_{11})_2Hg$: C, 49.26; H, 5.06. Found: C, 49.12; H, 4.86.

The recovery on crystallization from benzene-petroleum ether was not high. Subsequently ethyl acetate was found to be the solvent of choice, pure material being obtained in over 80% recovery.

A solution of the mercury derivative of nonadiyne-1,4 in ethyl acetate or in carbon tetrachloride darkens considerably on standing longer than one day.

(B) A sodium hydroxide solution was prepared according to Johnson and McEwen⁴ except that mercuric chloride was omitted. A homogenous mixture of 40 ml. of this alkaline solution with 2.30 g. of nonadiyne-1,4 (0.019 mole) and 50 ml. of 95% alcohol was allowed to stand for ten minutes at room temperature. Solid mercuric chloride (10.3 g.) was then added with vigorous stirring, followed after a few minutes by 100 ml. of water. Stirring was continued for a total of five minutes. The precipitate was collected, washed with water and air-dried. The tan derivative weighed 1.66 g. (42%) and melted at 107–111°. Three crystallizations from ethyl acetate brought the yield to 33% and the melting point to 110–111.5°.

Nonane from Nonadiyne-1,4.—A solution of partially hydrogenated nonadiyne-1,4 (total weight, 4.24 g.) in ethyl acetate was hydrogenated at room temperature over 100 mg. of platinum oxide catalyst until hydrogen was no longer absorbed. The amount of hydrogen taken up was close to the theoretical 4 moles. The catalyst was removed and washed in the filter with 60 ml. of sodium dry ether. The ether and ethyl acetate solvents were separated by distillation through a 20-cm. Vigreux column and the residue then fractionated. The fraction (2.87 g.) boiling at 147–149° (n_D^{25} 1.4031) on redistillation in a Claisen flask furnished 2.0 g. of water-white nonane, b.p. 148–149°. One further distillation gave nonane with n_D^{25} 1.4033. This compares well with the value, n_D^{25} 1.4034, observed at the same time for a sample of pure nonane obtained from National Bureau of Standards, as well as with reported values, *e.g.*, n_D^{25} 1.4031.²³ The recorded boiling point for nonane is 150.79° (760 mm.).²³ The infrared absorption curves for the hydrogenation product and for the authentic sample were for all practical purposes identical.

Ozonolysis of Nonadiyne-1,4.—Ozonized oxygen²⁴ was bubbled into a solution of nonadiyne-1,4 (5.843 g.) in 50 ml. of carbon tetrachloride (J. T. Baker Analyzed Reagent) cooled in an ice-bath. Approximately twice the theoretical amount of ozone was introduced in 5.25 hours. The reaction was mildly exothermic. The solution, containing an insoluble oil, was poured into a 500-ml. flask, the residual oil being transferred with the help of approximately 100 ml. of ethyl acetate. Ice-cold water (100 ml.) was added and the mixture was boiled under a condenser for 15 minutes. The organic layer was washed with two 25-ml. portions of water, and was treated with 50 ml. of 20% hydrogen peroxide. The mixture was warmed on the steam-bath for 0.5 hour, then cooled and shaken with 25 ml. of 10% sodium hydroxide solution. The aqueous layer was separated and

the organic layer was washed with two 25-ml. portions of 2% sodium hydroxide solution. The combined alkaline extracts were acidified with concentrated hydrochloric acid and extracted with three 50-ml. portions of petroleum ether (b.p. 35–75°). The petroleum ether extract, after drying over calcium chloride, was distilled to remove solvent. Distillation of the residual oil (2.6 g.) at 172–184° afforded 2.0 g. of water-white valeric acid, n_D^{25} 1.4059. The boiling point was determined as 182–184°. These constants should be compared to the boiling point (186.05° at 760 mm.) and the index of refraction (n_D^{25} 1.4064) reported for valeric acid in the Dreisbach-Dow Chemical Co. compilation of data.

The neutralization equivalent (101.5) compared well with the theoretical value for valeric acid (102).

The anilide, prepared from the acid chloride and aniline, melted at 60.5–61.8°. The anilide of valeric acid melts at 63°. ²⁵

Deuteration of Nonadiyne-1,4.—Nonadiyne-1,4 (10.36 g. or 0.080 mole) with n_D^{25} 1.4504 was boiled and stirred under purified nitrogen with ethereal ethylmagnesium bromide (from 2.4 g. or 0.10 g. atom of magnesium and 10 ml. of ethyl bromide) for 1½–2 hours. The nitrogen under slight pressure was then used to force the cooled solution from the flask directly into 10 ml. of ice-cold deuterium oxide (99.5%) into which 4 g. of phosphorus oxychloride had been dissolved. The reaction was strongly exothermic, and much ether was lost. The resulting mixture, after vigorous agitation, was filtered through a sintered glass funnel. The ether layer was washed four times with 10-ml. portions of deuterium oxide, and was dried over magnesium sulfate. Distillation through a 6" Vigreux column afforded 6.4 g. of material, b.p. 37–38° (1 mm.), n_D^{25} 1.4503. An appreciable absorption at 3.02 μ showed that deuteration at the acetylenic hydrogen position was not complete. Accordingly the entire process was repeated to give colorless product with b.p. 36–37° (1 mm.) and n_D^{25} 1.4505.

To check the possibility of rearrangement during the deuteration process, the Grignard reagent of nonadiyne-1,4 was treated as above, but with ordinary water. The infrared absorption spectrum of this regenerated nonadiyne (n_D^{25} 1.4503) was identical with that of the original material except for a slight increase (estimated at about a 6% decrease in transmission) in the intensity of the 5.15 μ peak, and a similar increase in the intensity of the band at 11.76 μ . Figure 2 compares the infrared curves in the low wave length region of twice-deuterated nonadiyne-1,4 with this regenerated nonadiyne-1,4.

Dodecatriyne-1,4,7.—After removal of most of the nonadiyne-1,4 from the product obtained in the coupling of hexynylmagnesium bromide and propargyl bromide (see above), distillation was continued under lower pressure. A steady boiling point of 89–90° (1 mm.) was noted for a 3.9-g. fraction of colorless distillate, n_D^{25} 1.4994. The yield based on propargyl bromide used was 9.1%; in other experiments the yields were 7.2, 9.5 and 14.3%, and the index of refraction (n_D^{25}) was 1.4958 and 1.4954.

The above product was redistilled, and was collected in several ampoules, which were sealed under vacuum and submitted for analysis.

Anal. Calcd. for $C_{12}H_{14}$: C, 91.07; H, 8.91. Found for material with b.p. 112–113° (3–4 mm.) and n_D^{25} 1.4945: C, 89.8; H, 8.7. Found for material boiling at 100° (2 mm.): C, 90.2, 90.6; H, 8.7, 8.8. Found for material with b.p. 56–57° (0.04 mm.) and n_D^{25} 1.4994: C, 90.27; H, 8.63.

The analysts' reports stated that color developed in the samples immediately after opening the ampoules. The analytical results as well as the development of color are readily accounted for by rapid combination of dodecatriyne-1,4,7 with atmospheric oxygen.

When mixed with alkaline mercuric iodide, dodecatriyne-1,4,7 gave a precipitate, which, however, could not be purified by crystallization.

Dodecane from Dodecadiyne-1,4,7.—Dodecatriyne-1,4,7 (0.793 g. or 0.0050 mole) in solution with 25 ml. of ethyl acetate was hydrogenated over 50 mg. of platinum oxide catalyst. Hydrogenation proceeded smoothly, 95.2% of the expected six moles of hydrogen being absorbed. The mixture was filtered, the catalyst was washed with 10 ml. of

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

(24) L. I. Smith, F. L. Greenwood and O. Hudrlik, *Org. Syntheses*, **26**, 63 (1946).

(25) N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," Thomas Y. Crowell Co., New York, N. Y., 1947, p. 358.

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_D^{25} 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,²⁸ respectively, as 216.27° (760 mm.) and n_D^{25} 1.4195.

BOSTON, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF BOSTON UNIVERSITY]

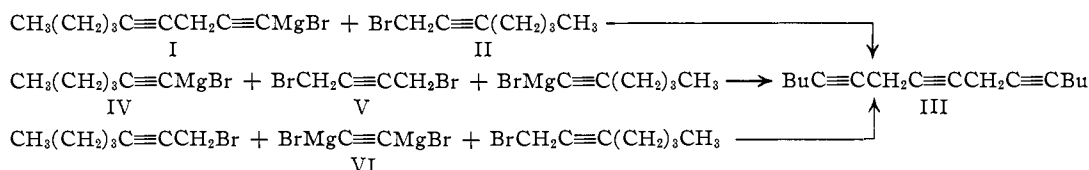
Hexadecatriyne-5,8,11

BY WALTER J. GENSLER AND A. P. MAHADEVAN

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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 coupling¹ of the Grignard derivative (I) of nonadiyne-1,4² 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.



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 $m\mu$ (ϵ approx. 450) and at 272 $m\mu$ (ϵ 480–580). However, neither the characteristic collection of maxima at 210–266 $m\mu$ shown by conjugated acetylenes⁶ nor the high intensity absorption below 235

$m\mu$ shown by ene-yne⁶ 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.

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Experimental⁷

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_D^{25} 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

(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.

(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.