[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF BOSTON UNIVERSITY]

Preparation and Structure of Tridecadiyne-5,8

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Cuprous compounds were found to be the only materials effective as catalysts in the formation of tridecadiyne-5,8 from hexynylmagnesium bromide and 1-bromoheptyne-2. The precipitate deposited in such reactions is hexynylcopper. The structure of the tridecadiyne-5,8 has been established.

The preparation of tridecadiyne-5,8 (III) by reaction of hexynylmagnesium bromide (I) with 1-bromoheptyne-2 (II) is the subject of this communication. The work was undertaken as part of a project on skipped unsaturations,[2] tridecadiyne-5,8[3] being selected as a representative skipped diyne.

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

$$\underset{\text{III}}{CH_3(CH_2)_3C{\equiv}CCH_2C{\equiv}C(CH_2)_3CH_3}$$

Catalysts in the Reaction of Hexynylmagnesium Bromide and 1-Bromoheptyne-2.—The behavior of hexynylmagnesium bromide (I) in undergoing no significant reaction with 1-bromoheptyne-2 (II) even after many hours in boiling ether is consistent with the extraordinary inertness of acetylenic Grignard reagents toward propargyl bromides.[4] Knowing that cuprous salts catalyze the coupling process,[9] we examined other materials for similar and possibly enhanced catalytic activity. We found that cadmium chloride, silver nitrate, manganese(II) chloride and hexynylmercury(II),[10] in small amounts, had no effect in promoting the coupling of hexynylmagnesium bromide and 1-bromoheptyne-2. Magnesium bromide in amounts as high as 40–50 mole per cent. was likewise ineffective. Less than 10% of the titrable Grignard reagent was consumed in 20-hour reaction periods, and starting material in appreciable amounts was recovered. Cobalt(II) chloride and iron(II) chloride, although unusually active in catalyzing the consumption of Grignard reagent as well as of 1-bromoheptyne-2, furnished materials which were different from the desired coupling product III. Absorption in the 220–270 mμ region was more intense for these materials than for tridecadiyne-5,8. Also, their infrared absorption curves differed in a number of features from that of tridecadiyne-5,8, notably in the presence of peaks at 5.2 and at 6 μ.

Cuprous compounds were the only effective catalysts for the formation of tridecadiyne-5,8. Yields from 50 to 80% were obtained with small amounts of cuprous chloride, cuprous bromide, hexynylcopper,[11] and with the yellow precipitate that was deposited at the end of various copper-catalyzed coupline processes (*vide infra*). Although the highest yield of tridecadiyne-5,8 was obtained with cuprous chloride, the available data do not justify ordering the cuprous compounds as to relative efficacy. Cuprous chloride, potent in catalyzing the reaction of hexynylmagnesium bromide and 1-bromoheptyne-2, was without effect in the reaction of hexynylmagnesium bromide and methylene bromide. Evidently, even with cuprous copper, a certain degree of activity is demanded of the halide combining with the acetylenic Grignard reagent.

Constitution of Tridecadiyne-5,8 (III).—In arriving at the unequivocal assignment of structure III to the coupling product, three possibly complicating factors had to be taken into account. First, there is some question about the homogeneity of one of the reactants, the 1-bromoheptyne-2.[12] The troublesome feature is an unexplained absorption peak at 5.8 μ, possibly attributable to an allenic grouping. The 1-bromoheptyne-2 used in this work showed no allenic absorption in the 5.15 μ region either in carbon tetrachloride solution or neat in a 0.40 mm. cell. The above mentioned 5.8 μ band was marked (approximately 40% transmission) in the curve taken with the neat liquid but was negligible in the carbon tetrachloride solution. In view of the observation that cuprous bromide helps to catalyze the rearrangement of propargyl bromide to bromoallene[13] it was of some

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[2] We have long felt the need of a term applicable to unsaturation such as in linoleic acid, linolenic acid, pentadiene-1,4, allylacetylene, etc., that is, to *unsaturations separated by a single saturated atom.* Such a term would be helpful in focusing attention on the special properties as well as in referring to the general structure of this kind of unsaturation. We have found the word "skipped," which is descriptive and which seems appropriate, to serve satisfactorily. It is proposed that this word be used very much the same way that "conjugated" is used for unsaturations separated by a single bond. In addition, the atom between the two unsaturations could be referred to as a "skipped atom" or a "skipped position."

[3] G. F. Hennion and E. P. Bell, THIS JOURNAL, **65**, 1847 (1943).

[4] Tchao Yin Lai[5] found no combination of acetylenic Grignard reagents with propargyl bromides even in boiling toluene. Similarly Taylor and Strong[6] and also Gensler and Thomas[7] failed to effect the coupling until catalysts were added. The preparation, in 8% yield, of 1,5-diphenylpentadiyne-1,4 by coupling phenylacetylenemagnesium bromide with methylene iodide[8] must be attributed either to the special influence of the phenyl group or to the inadvertent presence of a catalyst (cuprous copper?). Hennion and Bell[3] observed no reaction between hexynylmagnesium bromide and methylene bromide.

[5] Tchao Yin Lai, *Bull. soc. chim.*, [4] **53**, 1537 (1933).

[6] W. R. Taylor and F. M. Strong, THIS JOURNAL, **72**, 4263 (1950).

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

[8] V. Grignard and L. Lapayre, *Compt. rend.*, **192**, 250 (1931); *Bull. soc. chim.*, [4] **43**, 141 (1928).

[9] *Cf.* references 6 and 7. Also see H. M. Walborsky, R. H. Davis and D. R. Howton, THIS JOURNAL, **73**, 2590 (1951). Hennion and Bell[3] used cuprous chloride in the reaction of hexynylmagnesium bromide with methylene sulfate to form (13% yield) tridecadiyne-5,8. However no comment is made on the possibility of the reaction with methylene sulfate occurring in the *absence* of cuprous chloride. At least one propargyl sulfonate has been successfully coupled with an acetylenic Grignard reagent without added catalyst (R. A. Raphael and F. Sondheimer, *J. Chem. Soc.*, 2100 (1950)).

[10] *Cf.* T. H. Vaughn, THIS JOURNAL, **55**, 3453 (1933); H. J. Hall and G. B. Bachman, *Ind. Eng. Chem.*, **28**, 57 (1936).

[11] Analytically pure $CH_3(CH_2)_3C{\equiv}CCu$. Hexynylcopper was previously reported by H. Van Risseghem, *Bull. soc. chim. Belg.*, **35**, 328 (356) (1926).

[12] J. H. Wotiz and co-workers, THIS JOURNAL, **71**, 3141 (1949); **72**, 5055 (1950); **73**, 693 (1951); **75**, 4856 (1953).

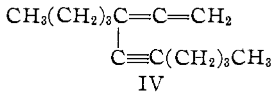
[13] T. L. Jacobs and W. F. Brill, *ibid.*, **75**, 1314 (1953).

interest to find that a sample of 1-bromoheptyne-2 recovered from a cuprous catalyzed coupling reaction showed no allenic absorption at 5.15 μ, although a new peak had developed at 5.87 μ.

Second, allenes have been observed among the coupling products of propargyl halides with Grignard reagents. Many replacement reactions with propargyl halides, including coupling with Grignard reagents, give products in which the absence of the allene grouping is either proved or assumed.[9,14] However, the reports that Grignard coupling *can* lead to allenic products[15] made any *a priori* assignment of a non-allenic structure to the tridecadiyne-5,8 questionable.

Third, there was no assurance that the skipped diyne product once formed would be resistant to acetylenic–allenic isomerization either in the reaction mixture or during the isolation. Although the interconversion, essentially a prototropic shift, occurs generally under the influence of a strong base and at elevated temperatures,[7,16] this is not always the case. In some compounds acetylenic-allenic prototropy is relatively facile.[17] Accordingly, this kind of change in tridecadiyne-5,8 even under the mild conditions of its formation or of its isolation could not be disregarded. Particular structures that came into consideration as a result of these isomerization possibilities are allenes IV and V and diyne VI.

From the fact that hydrogenation of tridecadiyne-5,8 yielded *n*-tridecane, all possibilities with branched chains, for example IV, could be eliminated. Ozonolysis of tridecadiyne-5,8 yielded valeric acid. Consequently no unsaturation could be present closer than five carbons to either end of the chain. These two conditions limited the possibilities to tridecadiyne-5,8 (III) itself, to the allene–acetylene V, and with a rather low degree of likelihood to the conjugated diyne VI.



$CH_3(CH_2)_3C(C{\equiv}C(CH_2)_3CH_3){=}C{=}CH_2$

IV

$CH_3(CH_2)_3C{\equiv}CCH{=}C{=}CH(CH_2)_3CH_3$

V

$CH_3(CH_2)_3C{\equiv}CC{\equiv}CCH_2(CH_2)_3CH_3$

VI

A choice based on molar refraction was only partially successful. The molar refraction of the skipped diyne III, as calculated from tables of bond values, is 58.90; that of the conjugated diyne VI is greater than 58.90; and that of the allene–acetylene V is greater than 59.70.[18] Comparison with 58.85, the observed molar refraction for the coupling product, spoke strongly against structure V, but was of limited value in deciding between structures III and VI.

The absorption spectra of the coupling product supported structure III. The ultraviolet absorption curve with a single maximum of low intensity at 271 mμ (ϵ 204) had none of the features expected of a conjugated diyne[19,20,21] (as in VI), or of a conjugated ene–yne[20,22] (as in V[23]), but could well be compatible with a skipped diyne (as in III). Actually even this low intensity maximum at 271 mμ may be a feature not so much of the skipped diyne as of a transformation (oxidation?) product. The possibility was suggested by the dependence of the intensity of the 271 mμ band on the history of the sample used. For example, the lowest intensity at this point (λ_{max} 269 mμ, ϵ 175) was observed with a sample of tridecadiyne-5,8 that had just been distilled (b.p. 78–79° (0.4 mm.); $n^{25}D$ 1.4614). Another sample of tridecadiyne-5,8 ($n^{25}D$ 1.4620) gave a curve with λ_{max} 270 mμ, ϵ 343. To try the effect of exposure to air, tridecadiyne-5,8 was allowed to stand open for three days. Redetermination of the absorption curve showed that the general shape was the same but that the entire curve was displaced upwards (λ_{max} 270 mμ, ϵ 2760). In the light of these observations the absorption of the skipped diyne system on the high wave length side of 220 mμ may prove to be free of maxima.[24]

The infrared absorption of the tridecadiyne-5,8 (note the accompanying curve) admits the possibility of only a very low content of allene if any at all, for the transmittance through a 0.4 mm. layer of the neat liquid at the characteristic allene absorption region, that is, at 5.1–5.2 μ,[25] is approximately

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(14) See, *inter alia*, J. R. Johnson, T. L. Jacobs and A. M. Schwarz, THIS JOURNAL, **60**, 1885 (1938); K. N. Campbell and L. T. Eby, *ibid.*, **62**, 1798 (1940); Fr. Moulin, *Helv. Chim. Acta*, **34**, 2416 (1951); Tchao Yin Lai, *Bull. soc. chim.*, [4] **53**, 1537 (1933); A. W. Johnson, *J. Chem. Soc.*, 1009 (1946); R. Ya. Levina and Yu. S. Shabarov, *Doklady Akad. Nauk S.S.S.R.*, **84**, 509 (1952) (*C.A.*, **47**, 3219 (1953)).

(15) *Cf.* M. Gaudemar, *Compt. rend.*, **232**, 1945 (1951); A. I. Zakharova and R. A. Sapozhnikova, *Zhur. Obshcheĭ Khim.*, **22**, 1804 (1952) (*C. A.*, **47**, 6857 (1953); A. I. Zakharova, *ibid.*, **19**, 1297 (1949) (*C. A.*, **44**, 1000 (1950)); A. N. Pudovik and L. A. Mukhamedova, *ibid.*, **21**, 1472 (1951) (*C. A.*, **46**, 4467 (1952)); C. Prévost, M. Gaudemar and J. Honigberg, *Compt. rend.*, **230**, 1186 (1950).

(16) M. Bourguel, *ibid.*, **192**, 686 (1931); T. L. Jacobs, R. Akawie and R. G. Cooper, THIS JOURNAL, **73**, 1273 (1951); E. F. Zeberg, *J. Gen. Chem.* (*U.S.S.R.*), **5**, 1016 (1935); (*C. A.*, **30**, 1023 (1936)); R. C. Lord and P. Venkateswarlu, *J. Chem. Phys.*, **20**, 1237 (1952).

(17) E. R. H. Jones and co-workers, *J. Chem. Soc.*, 3197, 3201, 3208, 3212 (1954); W. Oroshnik, A. D. Mebane and G. Karmas, THIS JOURNAL, **75**, 1050 (1953); W. D. Celmer and I. A. Solomons, *ibid.*, **75**, 3430 (1953); G. F. Hennion and J. J. Sheehan, *ibid.*, **71**, 1964 (1949); H. H. Schlubach and V. Wolf, *Ann.*, **568**, 141 (1950). 1,3-Diarylpropynes isomerize readily to allenes over alumina but not under other conditions (J. R. Johnson, T. L. Jacobs and A. M. Schwarz, THIS JOURNAL, **60**, 1885 (1948); T. L. Jacobs and S. Singer, *J. Org. Chem.*, **17**, 475 (1952).

(18) The figures were arrived at from the structures of III, V and VI by making use of the bond values of A. Vogel, *et al.*, *J. Chem. Soc.*, 514 (1952). In the allene-acetylene system V, the contribution of the cumulated double bonds was taken as twice that of an ordinary isolated double bond. There is some evidence, however, that the cumulated double bonds contribute approximately 0.44 unit more than two ordinary double bonds.[13] Furthermore, to this increase in the expected molar refraction for compound V should be added 1 unit, which is the exaltation associated with conjugation of a double and a triple bond (J. Cymerman-Craig, E. G. Davis and J. S. Lake, *J. Chem. Soc.*, 1874 (1954). For the diyne VI, conjugation should reflect in an increase in the molar refraction over that calculated for the non-conjugated skipped diyne III.

(19) F. Bohlmann, *Chem. Ber.*, **84**, 545, 785 (1951); **86**, 657 (1953).

(20) J. B. Armitage and M. C. Whiting, *J. Chem. Soc.*, 2005 (1952); J. P. Riley, *ibid.*, 2193 (1952).

(21) J. B. Armitage, *et al.*, *ibid.*, 1998 (1952).

(22) *Cf.* A. W. Johnson, "Acetylenic Compounds," Vol. I, E. Arnold and Company, London, 1946, p. 33 and 151; W. D. Celmer and I. A. Solomons, THIS JOURNAL, **75**, 3430 (1953).

(23) The ultraviolet chromophore in structure V is considered to be a triple bond conjugated to *one* double bond. See the discussion by W. O. Celmer and I. A. Solomons, *ibid.*, **75**, 1372 (1953).

(24) The absorption of the skipped *diene* and of the skipped en–yne systems in this region is similarly low.

(25) *Cf.* L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 52; N. Sheppard and D. M. Simpson, *Quart. Rev.*, **6**, 1 (1952); J. H. Wotiz and W. D. Celmer, THIS JOURNAL, **74**, 1860 (1952); T. L. Jacobs, R. Akawie and R. G. Cooper, *ibid.*, **73**, 1273 (1951).

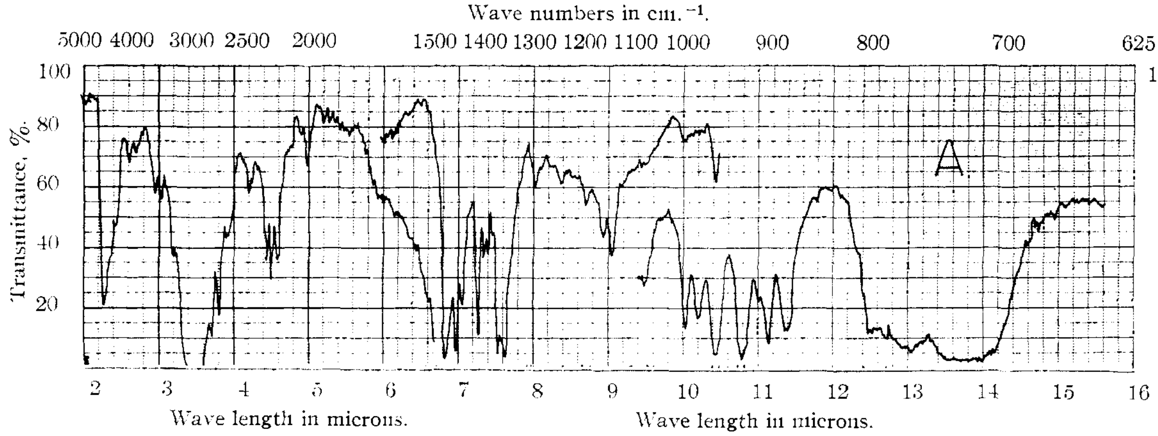

Fig. 1.—Infrared absorption curve for tridecadiyne-5,8 (n^{25}_{D} 1.4615) taken with a 0.40 mm. layer of liquid using a Baird double-beam spectrophotometer. The curve (A) refers to a solution of 100 mg. of the material plus 1 ml. of carbon tetrachloride *vs.* carbon tetrachloride.

94%. On this evidence alone, structure V could be definitely excluded. Although tridecadiyne-5,8 has only two triple bonds, the absorption curves show a cluster of *three* absorption bands (at 4.42, 4.49 and 4.57 μ) at the region characteristic of the C≡C stretching vibration.[26] This behavior is not without precedent, the appearance of extra satellite peaks in the 4.4 μ region of the absorption curves of acetylenes having been noted before.[26b]

Nature of the Precipitate Deposited During the Copper-catalyzed Coupling Reaction.—A yellow solid was observed to precipitate toward the end of the cuprous catalyzed combination of hexynylmagnesium bromide and 1-bromoheptyne-2.[7,27] The composition of samples of this solid obtained after hydrolyzing the reaction mixture varied considerably. When, however, the yellow precipitate was isolated by filtration directly from the Grignard reaction, analytical results were obtained that served to identify the material as hexynylcopper.[7]

The solubility behavior of the several copper catalysts is of interest. The materials are readily soluble in ethereal hexynylmagnesium bromide. However as the concentration of the Grignard reagent decreases—as for example, hexynylmagnesium bromide in the coupling reaction is depleted—the hexynylcopper tends to come out of solution. Where a large excess of hexynylmagnesium bromide is used in the coupling reaction no precipitate develops. That the *concentration* of Grignard reagent is the important factor could be shown by dissolving cuprous chloride in approximately one molar ethereal hexynylmagnesium bromide, and diluting the clear pale yellow solution tenfold with dry ether. The diluted solution gradually deposited yellow precipitate. Anhydrous cuprous chloride is entirely insoluble in an ether solution of 1-bromoheptyne-2. Clearly the ether solubility of hexynylcopper is associated with hexynylmagnesium bromide.

In considering the form in which hexynylcopper exists in ethereal hexynylmagnesium bromide, the experimental facts are consistent with the picture of an ether soluble complex of the two materials, possibly (neglecting ether of solvation) as $C_4H_9C{\equiv}\overset{(-)}{C}Cu{-}\overset{(+)}{Br}MgC{\equiv}CC_4H_9$. It is suggested that the propargyl bromide reacts with this kind of combination by way of a cyclic reaction complex[28] to form the coupling product, and simultaneously to release cuprous bromide and hexynylmagnesium bromide. Whatever the detailed mechanism, this copper-catalyzed coupling clearly is not related to the homolytic processes observed in other metal halide catalyzed Grignard reactions.[29] On the other hand the cobalt- and iron-catalyzed couplings, which are relatively rapid and which afford different products, may proceed by a radical mechanism.

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Experimental[30]

Tridecadiyne-5,8 from the Cuprous Chloride Catalyzed Reaction of Hexynylmagnesium Bromide and 1-Bromoheptyne-2.—No difference was evident in the results when ethylmagnesium bromide, which was used for the preparation of hexynylmagnesium bromide, was formed from shreds of sublimed magnesium[31] or from ordinary magnesium turnings. The magnesium was allowed to react with approximately 1.25 moles of ethereal ethyl bromide until

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[26] (a) Bellamy, ref. 25, p. 50; (b) J. H. Wotiz and F. A. Miller, THIS JOURNAL, **71**, 3441 (1949).

[27] A black precipitate, presumably copper, is formed when unreacted ethylmagnesium bromide is present.[7] The ethyl Grignard reagent forms ethylcopper, which in contrast to hexynylcopper decomposes spontaneously (*cf.* H. Gilman, R. G. Jones and L. A. Woods, *J. Org. Chem.*, **17**, 1630 (1952)).

[28] Cyclic reaction complexes have been proposed for other Grignard reactions (*cf.* C. G. Swain and H. B. Boyles, THIS JOURNAL, **73**, 870 (1951); R. T. Morrison and M. Wishman, *ibid.*, **76**, 1059 (1954).

[29] For example see M. S. Kharasch and M. Kleiman, *ibid.*, **65**, 491 (1943).

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

[31] We wish to thank The Dow Chemical Company for generous samples of this magnesium, which is considered to be free of all heavy metals except lead (M. S. Kharasch, *et al.*, THIS JOURNAL, **63**, 2305 (1941); R. T. Morrison and M. Wishman, *ibid.*, **76**, 1059 (1954)).

all the magnesium had dissolved. The Grignard solution was then filtered through a plug of glass wool either directly into another reaction flask, or into a graduated cylindrical separatory funnel for use as a stock solution. The concentration of the ethyl Grignard solution[32] was generally between one and two molar.

An ethereal solution of ethylmagnesium bromide (320 ml. containing *ca.* 0.6 mole) was transferred from a stock solution to a three-necked flask provided with a mercury sealed stirrer, a dropping funnel, and a condenser connected at the top through a calcium chloride tube to a line supplying dry nitrogen under a small pressure. The stirrer was in operation and nitrogen was maintained over the reaction mixture throughout the experiment. A solution of 49.2 g. (0.60 mole) of hexyne-1 in 50 ml. of sodium-dry ether was added to the solution at a rate rapid enough to cause slow reflux. After the addition, which required 45 minutes, the mixture was boiled for one hour. Dry cuprous chloride (1.0 g. or 0.01 mole) was then added, and the mixture was boiled further for 15 minutes. To the clear pale green solution was added over a 15-minute period a solution of 89 g. (0.508 mole) of 1-bromoheptyne-2[33] in 200 ml. of dry ether. After a few minutes, the level of the liquid in the flask was marked (or was brought to a volume calibration mark by addition of ether) and a 2-ml. (or a 5-ml.) aliquot removed for acid–base titration.[32] The mixture was boiled and stirred for 20 hours.

Aliquots for determination of Grignard content were removed at intervals during and at the end of the reaction period. If necessary, dry ether was added to bring the volume to the original mark. Where two layers had formed, the aliquot was taken from the upper layer (invariably the larger) and the calculations were made assigning the same Grignard content to the lower as to the upper layer. In the isolated experiments in which aliquots were taken from both layers, the lower layer was found to be higher in Grignard concentration than the upper.

In this particular experiment the initial total Grignard content was found to be 0.58 mole, and the final Grignard content 0.029 mole. The two-phase reaction mixture was poured over crushed ice containing sulfuric acid, and the mixture filtered. The ether layer was removed, washed with bicarbonate solution, and dried over anhydrous magnesium sulfate. The dry ether solution was boiled to remove solvent, and the residue distilled. A small all glass still provided with a 10-cm. Vigreux column and a "pig" for cutting fractions was used. In this experiment no fraction corresponding to recovered 1-bromoheptyne-2 was obtained. The yield of pale yellow tridecadiyne-5,8, boiling at 95° (1 mm.) and with $n^{25}\text{D}$ 1.4612, was 78.5 g., or 88% based on 1-bromoheptyne-2.

Constants for Pure Tridecadiyne-5,8.—Approximately 120 g. of tridecadiyne-5,8, pooled from various samples, was carefully distilled through a one-meter column, packed with helices and heated. After rejecting an initial portion, water-white tridecadiyne-5,8 boiling sharply at 63° (0.06 mm.) was collected. When the distillation was over but before the vacuum was broken, the flask, which had a long narrow neck, was cooled in a bath of trichloroethylene–solid carbon dioxide and was sealed. The flask was opened in an atmosphere of pure nitrogen.[34] The contents were distributed to several ampoules and test-tubes, which were then cooled and sealed still under nitrogen. The following data refer to this grade of tridecadiyne-5,8.

Anal. Calcd. for $C_{13}H_{20}$: C, 88.53; H, 11.46. Found: C, 88.6, 88.3; H, 11.5, 11.6; index of refraction, $n^{25}\text{D}$ 1.4615; density $d^{25}{}_4$ 0.82285. Molar refraction, calcd. for tridecadiyne-5,8 from bond values[18]: 58.896. Calcd. from the Lorenz–Lorentz equation: 58.85 (previously obsd. as 57.84[3]).

When pure, tridecadiyne-5,8 is a water-white liquid. However it is sensitive to oxygen and rapidly acquires a yellow, then a deeper color, in air.

Ozonolysis of Tridecadiyne-5,8.—Ozonized oxygen[35] was bubbled through a solution of 7.0 g. (0.04 mole) of tridecadiyne-5,8 in 80 ml. of carbon tetrachloride for 7.5 hours. The absorption tube was cooled periodically to keep the temperature close to 25°. The reaction mixture, after concentration *in vacuo*, was treated with 150 ml. of 30% hydrogen peroxide. From this oxidation mixture there could be obtained 4.5 g. of crude valeric acid with its characteristic odor. Distillation afforded the pure acid with b.p. 185–186° and $n^{22}\text{D}$ 1.4098. Valeric acid (No. 23-6 in the Dreisbach–Dow Chemical Company compilation of physical constants) has b.p. 186° and $n^{20}\text{D}$ 1.40846 and $n^{25}\text{D}$ 1.40640. The neutralization equivalent (100.0, 100.1) corresponded to that of valeric acid (102).

The anilide from this material melted at 62–63°. The melting point of the anilide of valeric acid is given as 63°.[36]

Tridecane from Tridecadiyne-5,8.—The ethyl acetate solution, pooled from several experiments in which the partial hydrogenation of tridecadiyne-5,8 (total weight 8.03 g.) had been studied, was stirred under an atmosphere of hydrogen in the presence of 0.3 g. of platinum oxide catalyst. Hydrogen absorption, initially rapid, became negligible after three hours. The total amount of hydrogen absorbed was estimated to be approximately 88% of the theoretical four moles. The catalyst was removed, rinsed on the filter with 50 ml. of ether, and the combined ethyl acetate and ether solutions freed of volatile solvents by distillation on the steam-bath. The residual liquid was distilled further to give 7.0 g. of tridecane, boiling at 232–233° and showing $n^{23}\text{D}$ 1.4234. The reported constants for tridecane are b.p. 235.4° and $n^{23}\text{D}$ 1.4242.[37]

Yellow Precipitate from the Copper-catalyzed Coupling.—A coupling reaction was carried out over a period of 40 hours using 50 ml. of (approximately) 2.3 molar stock solution of hexynylmagnesium bromide (*ca.* 0.115 mole), 22.5 g. (0.128 mole) of 1-bromoheptyne-2 in 25 ml. of ether and 0.5 g. of hexynylcopper. The reaction mixture, originally a pale green solution, contained a yellow precipitate after 24 hours. After the lower liquid layer was drained, the upper layer containing most of the solid was filtered through sintered glass under nitrogen. The solids were washed with dry ether, and were dried *in vacuo* for four hours. There was no loss in weight on drying this material for one hour *in vacuo* at 50°. The analytical results are as follows: (these values should be compared with those calculated for hexynylcopper, C_6H_9Cu: C, 49.75; H, 6.29; Cu, 43.93).

C	47.3	47.7	47.28	47.73
H	6.1	6.1	6.1	6.3
Cu (from CuO ash)	44.0	43.3	44.1	43.8
Halogen (as Br)	..	0.9	...	1.07

On ignition over an open flame on a porcelain crucible lid, the solid melted and then exploded. After further ignition the residue was leached with 6% sulfuric acid and then with hot concentrated hydrochloric acid. Addition of excess ammonia to the sulfuric acid extract resulted in a deep blue color; addition of hydrogen sulfide precipitated black cupric sulfide.

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[32] Concentrations were determined by acid–base titration in a manner similar to that described by H. Gilman, *et al.*, THIS JOURNAL, **45**, 150 (1923).

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

[34] We wish to thank Drs. G. R. Thomas and N. N. Lichtin for permission to use and for guidance in the operation of their "controlled atmosphere" apparatus (*Rev. Sci. Inst.*, **23**, 738 (1952)).

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

[36] N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," Thomas Y. Crowell Company, New York, N. Y., 1927, p. 358.

[37] G. Egloff, "Physical Constants of Hydrocarbons," Vol. V (Revised Values), American Chemical Society Monograph No. 78, Reinhold Publ. Corp., New York, 1953, p. 204.