[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

THE PREPARATION AND ALKYLATION OF METAL ACETYLIDES IN LIQUID AMMONIA*

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INTRODUCTION

In 1913 Lebeau and Picon[1] reported that 1-alkynes were produced in good yield by the action of certain alkyl iodides on sodium acetylide in liquid ammonia. The synthesis assumed importance when Picon[2] claimed that alkynes prepared by this method were extremely pure and free from products of rearrangement, and that the reaction was general for alkyl iodides as high as $C_{16}H_{33}I$.[3] The ease of manipulation and the ready availability of the necessary materials make this synthesis attractive, and it has accordingly been used by various investigators[4] for the preparation of the lower members of the acetylene series. Hurd and Meinert[5] have shown that the alkyl sulfates may be substituted for the alkyl iodides in the preparation of propyne and 1-butyne.

Lespieau and Journaud[6] have studied the action of allyl halides on sodium acetylide. The principal product is not pentenyne but a complex compound obtained by the action of two or more moles of allyl halide on each mole of sodium acetylide.

Recently Vaughn and Danehy[7] have shown that calcium acetylide may be used in this synthesis in place of sodium acetylide with comparable results.

The principal reaction occurring in this synthesis of alkynes and the only

* Paper XIX on the chemistry of alkyl acetylenes and their addition compounds; previous paper, *J. Am. Chem. Soc.*, **59**, 213 (1937).

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[1] LEBEAU AND PICON, *Compt. rend.*, **156**, 1077 (1913).

[2] PICON, *ibid.*, **158**, 1184, 1346 (1914).

[3] PICON, *ibid.*, **169**, 32 (1919).

[4] (*a*) MAAS AND RUSSELL, *J. Am. Chem. Soc.*, **43**, 1227 (1921); (*b*) HURD, MEINERT, AND SPENCE, *ibid.*, **52**, 1138 (1930); (*c*) HEISIG, *ibid.*, **53**, 3245 (1931); (*d*) TCHAO, *Bull. soc. chim.*, [4], **53**, 687 (1933).

[5] HURD AND MEINERT, *J. Am. Chem. Soc.*, **52**, 4540 (1930); **53**, 289 (1931).

[6] LESPIEAU AND JOURNAUD, *Bull. soc. chim.*, [4], **49**, 423 (1931).

[7] VAUGHN AND DANEHY, *Proc. Ind. Acad. Sci.*, **44**, 144 (1935).

one to which much attention has previously been directed is the simple action of the straight-chain alkyl compounds on sodium acetylide to yield the monoalkyl derivative,

$$RX + NaC{\equiv}CH \rightarrow RC{\equiv}CH + NaX$$

As we needed rather large quantities of alkynes for use in research projects, we have made over five hundred separate runs of this general type, and have prepared about 200 liters of alkynes, including 1-propyne, 1-butyne, 1-pentyne, 1-hexyne, 1-heptyne, 1-octyne, 1-nonyne, 1-decyne, and 1-hendecyne. In the course of this work we have applied the reaction to sodium, potassium, barium, and calcium acetylides and to alkyl chlorides, bromides, iodides, and sulfates. Certain improvements in technique have been devised, and a number of by-products, including acetylene, alkenes, alcohols, mono-, di-, and trialkylamines, dialkyl ethers, and dialkylethynes have been identified and their formation explained. Due to lack of space only a few selections from this mass of experimental data can be presented in this article.

PREPARATION AND PROPERTIES OF THE METAL ACETYLIDES

The synthesis of alkali and alkaline earth acetylides in liquid ammonia has usually been conducted by passing acetylene into a previously prepared solution of the metal or metal amide, reaction occurring according to the equations,

$$M + HC{\equiv}CH \rightarrow MC{\equiv}CH + \tfrac{1}{2} H_2$$
$$MNH_2 + HC{\equiv}CH \rightarrow MC{\equiv}CH + NH_3.$$

At ordinary pressure the first of these methods is much too slow for the preparation of large quantities of acetylides, while with the second difficulty is encountered in determining the end of the reaction. The preparation of sodium acetylide in an autoclave from sodium in liquid ammonia at room temperature and under acetylene pressures of 100 to 250 p.s.i. has been found to be more rapid. This method, however, has a number of disadvantages, the most important being the great danger of violent explosions, particularly unless air is completely displaced from all parts of the apparatus.

It was found that a far more rapid and satisfactory method for making the metal acetylides consisted in adding the blue solution of the metal in liquid ammonia to a solution of acetylene in liquid ammonia, with stirring and without allowing the entire body of the reacting solution to become blue at any time. Acetylene is apparently not very soluble in boiling liquid ammonia, but is markedly soluble at temperatures below the boiling point at atmospheric pressure, so that concentrated solutions may be

obtained either by precooling or by sweeping an excess of acetylene through the ammonia, thus cooling it by evaporation. We have observed that the presence of dissolved metal greatly decreases the rate and extent of solution of acetylene in liquid ammonia and thus retards the reaction. This effect of dissolved metal seems to be general for solutions of many gases in ammonia.

This manner of preparing metal acetylides results in the saving of considerable time. The conversion of 5 moles of sodium (dissolved in 2.5 liters of ammonia) by treatment with acetylene requires 5 to 7 hours for completion. The same amount of sodium may be converted to acetylide in 40 minutes by the new procedure.

The method works equally well with the metals sodium, potassium, calcium, and barium, and acetylides of all these metals[8] have been so prepared for use in this work. Samples of these acetylides were freed from ammonia by evacuation at room temperature and analyzed for metal

TABLE I

ANALYSES OF METAL 1-ACETYLIDES

ACETYLIDE	% OF METAL FOUND		% OF METAL CALCULATED
Sodium	47.55	47.65	47.92
Potassium	60.72	60.52	60.74
Calcium	44.80	44.20	44.44
Barium	82.38	84.12	73.40

content. An examination of Table I shows that with the exception of barium acetylide the compounds were very pure.

As expected, these metal acetylides were very unstable in air. The degree of their stability, however, varied considerably. Sodium and potassium acetylides, being the most stable, remain in white crystalline form for approximately 10 hours when exposed to dry air. Under similar conditions calcium acetylide is noticeably decomposed (brown color) after 5 hours. Our samples of barium acetylide were so unstable that they decomposed on standing for a few minutes, even in an atmosphere of ammonia.

Since, as will be shown later, no very significant differences in the reactivities of these acetylides were noted, the cheaper and more soluble sodium acetylide was used in most cases.

Since the total exclusion of air in the preparation of large quantities of sodium acetylide was not attempted, the material always contained some sodium hydroxide due to moisture occurring both in the air and in some

[8] MOISSAN, *Compt. rend.*, **127**, 911 (1898).

samples of commercial liquid ammonia, and it also undoubtedly contained small amounts of sodium oxide due to atmospheric oxygen. Traces of sodamide may also have been present in some cases since in the absence of excess acetylene, the reaction

$$NaNH_2 + HC{\equiv}CH \rightarrow NaC{\equiv}CH + NH_3$$

may be somewhat reversible. Some few preparations were carried out in iron vessels and in these there was no doubt but that a larger amount of sodamide, which was obtained by the action of ammonia on the metallic sodium in the presence of sodium oxide and iron salts,[9] was present. The acetylene used was from commercial cylinders and was usually passed through a porous alundum cup into concentrated sulfuric acid and then through a sodalime tower, thus removing practically all of the acetone, and obviating the presence of sodium acetone in the acetylide.

EXPERIMENTAL

Preparation of sodium acetylide.—Three (3) liters of liquid ammonia was placed in a 10-liter steel container and saturated with acetylene by bubbling the gas through the ammonia at a very rapid rate for 2 minutes. In a separate container a solution of 300 g. of sodium in 3 liters of liquid ammonia was prepared. This solution was added to the acetylene solution with stirring at such a rate that the entire mixture never became entirely blue at any time. If a slight excess of sodium was inadvertently added the solution was allowed to clear up completely, and was then treated with acetylene for 1 minute before continuation of the additions of metal solution. Ammonia was added as necessary to maintain the volume of the mixture.

Analysis of metal acetylides.—The metal acetylides were analyzed by determining the amount of base liberated upon hydrolysis with water. A small portion of the acetylide solution was taken, and the ammonia was removed from the sample by evaporation through a mercury trap at room temperature. After the sample had evaporated to dryness it was evacuated at room temperature until no more ammonia was evolved. In the case of some of the acetylides, such as barium and calcium, small amounts of impurities such as oxide, chloride, etc. were permitted to settle out of the reaction mixture before a sample was taken.

The dried samples of acetylide were ground by adding glass balls to the flask and rotating by hand for some time. In an atmosphere of nitrogen a sample of 0.1–0.2 g. of the acetylide was placed in a small sample bottle and weighed. The sample bottle was allowed to drop in an upright position into a 500-ml. Erlenmeyer flask containing about 150 ml. of previously boiled, distilled water. A rubber stopper was placed in the mouth of the Erlenmeyer flask, and the sample bottle was opened by shaking. After hydrolysis of the sample the shaking was continued for a few moments until the gas, smoky in appearance, had completely cleared. The basic solution was then titrated with decinormal acid, with phenolphthalein as an indicator. To insure against the presence of ammonia the titrated solutions were treated with an excess of standard base, boiled for ½ hour, and then back-titrated. No ammonia was found in any case.

[9] VAUGHN, VOGT, AND NIEUWLAND, *J. Am. Chem. Soc.*, **56**, 2120 (1934).

In the analysis of calcium and barium acetylides, 25 ml. of decinormal acid was added to the water used in hydrolysis and the analysis then completed by back-titrating with decinormal sodium hydroxide.

REACTION OF SODIUM ACETYLIDE WITH ALKYL HALIDES AND ALKYL SULFATES IN LIQUID AMMONIA

The reaction of sodium acetylide with a number of alkyl halides has been carried out under a great variety of conditions, and the effect of some of these variables may be stated as follows.

The reactivity of the alkyl halides increases with the atomic weight of the halogen and decreases with the increasing size of the alkyl group, possibly due to the decreasing solubility in liquid ammonia. The reaction with alkyl sulfates is much more rapid than with any of the alkyl halides. Alkyl bromides are in general the most satisfactory for this reaction because they react more rapidly than alkyl chlorides and give smaller quantities of amine by-products than either the iodides or sulfates, and for other reasons which will be given below.

Some of the runs were made in an autoclave at room temperature and above and at pressures of 100 to 250 p.s.i.; some were made at atmospheric pressure and temperatures slightly above −34°C., while still others were made at 25 p.s.i. pressure in an aluminum pressure cooker. Higher temperatures increased the rate of the principal reaction and also that of some of the side reactions such as the formation of alkylamines from ammonia and the alkyl halides. Use of the autoclave obviated a part of the loss of liquid ammonia and of volatile products and by-products by evaporation, although some loss did occur when the pressure in the autoclave was released. A somewhat better recovery of products could be obtained by venting the autoclave through a condenser cooled by liquid ammonia.[10] The final yield of 1-alkynes in a number of cases appeared to be somewhat higher‡ at −34°C. than at higher temperatures.

EXPERIMENTAL

The two experiments that follow may be considered typical of those run at atmospheric and super-atmospheric pressures, respectively.

Preparation of 1-hexyne at atmospheric pressure.‡—Ninety (90) grams of sodium was converted to acetylide in a 5-liter 3-necked flask equipped with a high-speed, mercury-sealed stirrer and a gas-inlet tube, by the procedure previously described.

‡ Mr. Stefan J. Slanina, who devised this modified procedure, has recently demonstrated that this procedure is capable of producing 80 per cent. yields of hexyne and heptyne in an over-all time of four hours. The essential modifications comprise very effective stirring and recovery of volatile and entrained material. Entrainment may be markedly minimized by mounting a second liquid ammonia-cooled condenser of the coil type above the bulbed condenser.

The gas-inlet tube was then replaced with a dropping funnel, and a liquid-ammonia-cooled reflux condenser[10] was put into place. Then 413 g. of butyl bromide was slowly added during a period of 2.25 hours. During the addition of the bromide it was necessary to add an additional liter of ammonia to maintain the volume of the solution. After stirring for 2.5 hours after the final addition of butyl bromide, during which time it was necessary to add 2 liters of liquid ammonia, the reaction mixture was hydrolyzed by the dropwise addition of 750 ml. of water, the hydrolysis requiring 1.5 hours. The reaction mixture separated into 2 layers, the upper of which was removed, washed with 10% hydrochloric acid until acid to litmus, then with 2% sodium carbonate, and, finally, twice with water. The product, weighing 200 g., was dried over calcium chloride and carefully fractionated through an efficient total condensation column (packed with glass spirals), 1 m. long and 1 cm. in diameter, using a reflux ratio of 10:1. After three fractionations the following fractions were collected:

(1)	70–72°	137 g.
(2)	72–98°	12 g.
(3)	98–102°	15 g.
(4)	residue	25 g.

A bromide analysis of fraction 1 by the sodium-liquid-ammonia method[11] showed that 0.88% of butyl bromide was present. The hexyne is equivalent to a 55.7% yield while the recovery of butyl bromide is 3.7%. By careful fractionation of the residue, 10 g. of dibutyl ether and 10 g. of 5-decyne boiling at 172–5°, were obtained.

Preparation of 1-heptyne in autoclave.—Twelve moles of sodium acetylide suspended in 3 liters of ammonia in a 10-liter steel autoclave, was treated with 12 moles of normal amyl chloride previously cooled by mixing with a small quantity of liquid ammonia. The head of the autoclave was made up as rapidly as possible and stirring started. During 4 hours the pressure gradually rose to 160 p.s.i., this being equivalent to a temperature of about 30°. The pressure was then slowly released, and the reaction mixture was hydrolyzed by addition of water until vigorous bubbling no longer occurred. The top layer which separated was removed, washed with water, dilute hydrochloric acid, and again with water. After drying over calcium chloride the crude product was combined with the product from another run of 11.5 moles and fractionally distilled through a column (packed with glass spirals) 1 m. long and 4 cm. in diameter, using a reflux ratio of 10:1. The following fractions were obtained:

(1)	41–50°	4.5 g.
(2)	50–97°	86 g.
(3)	97–98°	74 g.
(4)	98–99°	1150 g.
(5)	99–100°	187 g.
(6)	100–103°	142 g.
(7)	103–106°	72 g.
(8)	106–115°	84 g.
(9)	residue	104 g.

An analysis of fraction 4 indicated that 5.92% amyl chloride was present. This fraction therefore contained 1082 g. of heptyne, equivalent to a yield of 52.5%. By taking into account the heptyne contained in the other fractions boiling between 50 and 98°, and 99 and 103° the total yield is raised to the order of 60%.

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[10] VAUGHN AND POZZI, *J. Chem. Educ.*, **8**, 2433 (1931).

[11] VAUGHN AND NIEUWLAND, *Anal. Ed., Ind. Eng. Chem.*, **3**, 274 (1931).

In the preparation of propyne and butyne all runs were made at atmospheric pressure. Various procedures were used for the collection of the alkyne, depending on whether or not it was desired as a gas, in solution, or as a liquid. A typical large-scale procedure will be described.

Preparation of propyne—Apparatus.—A cylindrical steel reaction chamber measuring 15 x 30 in. with a capacity of 23 gal. was used for this preparation. The bottom of this vessel was fitted with a 1.5-in. gate valve to facilitate cleaning, and a 0.5-in. line for the admission of acetylene. A spare 0.5-in. line was also run into the lower side of the vessel so that acetylene might be introduced should the bottom line become clogged. The upper side of the vessel was fitted with a 0.5-in. line for the exit of gases and a 1-in. gate valve for safety release. The removable head of the vessel was fitted with a stirrer driven by a 0.25-H.P. motor. The head also bore a pressure gage and was fitted with a sight glass and a 2-liter dropping funnel that protruded 6 in. into the reaction chamber. This funnel, which was used for the introduction of liquids into the closed reactor, was kept under constant pressure by means of compressed air acting against a column of mercury, in order that materials might be forced into the vessel against slight pressure. The head assembly was fastened to a block and tackle in order that it might be readily lifted and handled.

Although the reaction was run at −34°C. the vessel was not insulated. It was found that the frost formed from the moisture in the air made a rather efficient insulator and that after the vessel had once been cooled, ammonia losses were rather small. The reaction vessel was mounted in a shallow pan which served to collect the melted frost at the end of a run.

The exit gas line of the reactor was connected with a washer which was made from a 22-liter Pyrex flask. The inlet tube of this washer terminated in a perforated bulb which served to break up the gas stream and facilitate washing. In addition to the exit tube for gases, this washer was fitted with an inlet and outlet tube for the wash water which was constantly changed during the run. The gas from this aqueous wash was passed through a vapor trap held at 20° and then into a 2.5-liter wash bottle containing 25% sulfuric acid and an indicator. The exit from the sulfuric acid bottle was connected to an ice-cooled trap and then to three 36 x 2 in. towers connected in series and containing, in order, sodalime, calcium chloride and potassium hydroxide. A mercury manometer, arranged so as to ring an alarm bell in case of a sudden pressure rise, was inserted in the gas line just ahead of the three towers. The outlet from the potassium hydroxide tower was connected to a condenser made up of fifteen 6-in. turns of 0.5-in. black iron pipe. The bottom of this spiral was connected to a 3-liter flask carrying a vent tube, and the entire assembly suspended in a 12 x 22-in. insulated tin container, which was filled with dry ice and acetone.

Process.—After the head of the reactor had been raised out of the way, liquid ammonia was run directly into the reaction vessel from a cylinder mounted on a dolly. Acetylene from a low-pressure generator was passed through a calcium chloride dryer and then admitted through the acetylene inlet, and the ammonia was saturated. During the saturation of the ammonia a solution of sodium metal in ammonia was made up in a separate container. While the passage of acetylene was continued this solution of sodium metal was added to the reaction vessel at such a rate that the entire solution never became blue due to the presence of excess sodium. During the metal addition the mixture was stirred by hand, and when foaming occurred a portable motor-driven stirrer was employed. Attempts were made to add the sodium metal in chunks but it was found that the conversion to acetylide was much slower than was the case with solutions, and considerable trouble due to foam-

ing was encountered. The solution process was highly satisfactory when properly conducted. In converting the sodium to sodium acetylide the end-point was readily determined by noting the disappearance of the blue color of sodium. In every case this end-point was rather carefully observed in order to avoid an excess of acetylene in the solution.

The head was then lowered into place and bolted down. The stirrer was started, and the mixture was allowed to stand from 1 to 2 hours in order to eliminate ethylene and any slight excess of acetylene that might be present. This ethylene, formed from the hydrogen liberated during the preparation of the acetylide, was not present to any large extent but it was necessary to allow time for its removal.

After the elimination of ethylene, the gas exit of the reactor was connected with the washing, drying, and condensing system, and methyl sulfate was added through the separatory funnel at a rate as rapid as the washing system would permit. Propyne was produced and came off with ammonia. Most of this ammonia was removed by the aqueous wash and the remainder by the sulfuric acid washes. A certain loss of propyne occurred during the washing with water, but this was unavoidable. After leaving the sulfuric acid washers, the propyne, which now contained as impurities water vapor and sulfuric acid spray, was passed through the cooled trap to remove the bulk of the entrained acid solution. The gas was then passed through sodalime to complete this removal. Water was then removed by the calcium ehloride and potassium hydroxide towers and the propyne was condensed in the carbon dioxide-acetone cooled condenser.

In a typical run of this sort 1200 g. of sodium was converted to acetylide with the use of 18 kg. of liquid ammonia. The solution was then diluted with 30 kg. of ammonia, and 8.5 kg. of dimethyl sulfate was added during 6.5 hours. A yield of 1596 g. of crude propyne, equivalent to 83% of the theoretical yield, was obtained. The purification of this propyne by low-temperature rectification indicated that the principal impurity was acetylene which was present to the extent of about 17%. This gives a corrected yield of 69% of the theoretical.

DISCUSSION

In Table II the yields of alkynes, from what may be regarded as typical experiments, are tabulated. Data on various combinations of acetylides and halides are given. Yields are not strictly reproducible, even within the limits given, but major deviations are not often met with in any given series of runs. The variations indicated in the table are largely due to the various methods of isolation and in part to the formation of by-products.

The yields of alkynes as indicated in Table II are so low that even by taking into account the formation of by-products (to be discussed later) it is evident that losses are encountered at some stage in the procedure. Since loss is most likely to occur during the hydrolysis and separation of the reaction mixture, experiments were conducted in which known amounts of alkynes were dissolved in liquid ammonia and immediately treated with sufficient water to stop boiling at room temperature. The alkyne was then recovered and the loss determined.

The solubility of 1-hexyne in concentrated aqueous ammonia was deter-

TABLE II

YIELDS OF 1-ALKYNES

METAL ACETYLIDE	ALKYL COMPOUND	YIELD ± 5%
Sodium	$(CH_3)_2SO_4$	100[a, e, i]
Sodium	$(CH_3)_2SO_4$	40[b, e]
Sodium	$(CH_3)_2SO_4$	69[g, e]
Sodium	$(C_2H_5)_2SO_4$	100[a, e, i]
Calcium	$(C_2H_5)_2SO_4$	100[a, e, i]
Potassium	$(C_2H_5)_2SO_4$	100[a, e, i]
Sodium	$(C_2H_5)_2SO_4$	52[c, e]
Calcium	$(C_2H_5)_2SO_4$	75[c, e]
Sodium	n-C_3H_7Br	44[c, e]
Sodium	i-C_3H_7Cl	0[f]
Sodium	i-C_3H_7Br	0[e]
Sodium	n-C_4H_9Br	47[f]
Sodium	n-C_4H_9Br	53[d]
Sodium	n-C_4H_9Br	56[e]
Sodium	n-C_4H_9Br	80[e, h]
Calcium	n-C_4H_9Br	45[f]
Sodium	n-$C_5H_{11}Cl$	53[f]
Calcium	n-$C_5H_{11}Cl$	56[f]
Sodium	n-$C_5H_{11}Br$	56[f]
Potassium	n-$C_5H_{11}Br$	54[f]
Calcium	n-$C_5H_{11}Br$	31[f]
Barium	n-$C_5H_{11}Br$	41[f]
Sodium	n-$C_5H_{11}Br$	50[d]
Sodium	n-$C_5H_{11}Br$	50[e]
Sodium	n-$C_5H_{11}Br$	80[e, h]
Sodium	n-$C_6H_{13}Br$	40[f]
Sodium	*cyc.*-$C_6H_{11}Br$	0[f]
Sodium	n-$C_7H_{15}Br$	46[f]
Sodium	n-$C_8H_{17}Br$	53[f]
Sodium	n-$C_9H_{19}Br$	51[f]
Sodium	C_6H_5Cl,Br,I	0[d, e, f]
Sodium	$CH_2:CHCl$	0[e, f]
Sodium	$C_6H_5CH_2Cl$	0[f, j]

[a] Collected as gas.

[b] Absorbed in ether at −34°.

[c] Passed through ammonia condenser and liquefied.

[d] Reaction conducted at 25 lb. pressure.

[e] Reaction conducted at atmospheric pressure.

[f] Reaction conducted in autoclave and allowed to come to room temperature.

[g] Liquefied by condenser cooled with solid CO_2-acetone.

[h] See footnote ‡.

[i] Yield based on volume of gaseous product soluble in alkaline mercuric cyanide solution.

[j] Product was a greenish waxy solid,—evidently a mixture of polymers of 3-phenyl-1-propyne.

mined by adding 20 ml. of the compound to a solution made by adding 100 ml. of water to 100 ml. of ammonia and vigorously agitating the mixture. On standing, 19.5 ml. of the alkyne separated, indicating that the solubility of the compound was less than 2.5 per cent. of the amount taken. This experiment was repeated several times with similar results.

That the solubility of alkynes in concentrated aqueous ammonia is low is further demonstrated by the fact that ether extraction of the aqueous layer resulting from the hydrolysis of reaction mixtures does not result in the recovery of substantial amounts of alkynes.

From these data it is evident that the large losses shown in Table III are due to vaporization and entrainment during the addition of the water. Losses are also sustained during release of the pressure on the autoclave after a run at superatmospheric pressures. By passage of the gases (ammonia, acetylene, and alkyne) from the autoclave through water and then

TABLE III

RECOVERY OF ALKYNES FROM LIQUID AMMONIA SOLUTIONS

ALKYNE	AMMONIA (ML.)	ALKYNE RECOVERED (ML.)	LOSS, %
20 ml., 1-Hexyne	150	12.75	37
50 ml., 1-Hexyne	250	32.5	35
50 ml., 1-Hexyne	250	39.0	32
50 ml., 1-Heptyne	250	44	12
50 ml., 1-Heptyne	250	44[a]	12
50 ml., 1-Heptyne	250	43.5[b]	13

[a] Water (250 ml.) added dropwise.

[b] Water (250 ml.) added as rapidly as possible.

through an ammonia-cooled condenser[10] a sufficient amount of alkyne could be recovered to increase the yields by 2 to 7 per cent., depending on the particular alkyne.

In attempts to improve yields many variations in conditions attending the preparation of hexyne and heptyne from sodium acetylide and the appropriate bromide were made, and their effect on the reaction determined. A discussion of some of this work will be given.

Volume of solution.—Best results were obtained when 0.5 to 1.0 liter of ammonia was present for every mole of sodium acetylide. The use of smaller amounts of ammonia lowered the yield by reducing the extent of reaction. This is shown by the recovery of large amounts of alkyl bromide from these runs. Larger amounts of ammonia lowered the yield by increasing the amount of loss due to vaporization and entrainment.

The presence of adequate amounts of ammonia during hydrolysis was

necessary to prevent rearrangement of the alkyne by the concentrated (and in extreme cases, hot) sodium hydroxide[12] produced. While preparing 1-hexyne, Hurd[13] observed that addition of water to the crude reaction product *after* removal of ammonia gives a product boiling at 71–72°, but containing only 79 per cent. of hexyne. It is likely that the impurities are rearranged products.

Time of reaction.—Several experiments were run at atmospheric pressure with moderate agitation to determine the optimum time of reaction. Data from these experiments are given in Table IV. All variables other than time of reaction were, of course, stabilized during these experiments.

These data indicate that 2 hours is sufficient time for reaction to occur to its maximum extent at atmospheric pressure, and that longer standing results in loss of alkyne by evaporation and entrainment.

In experiments run in the autoclave maximum reaction seemed to take place within the time the reaction mixture required to rise to room temperature. In preparative work, however, we have customarily allowed such mixtures to stand for at least 30 minutes before reducing the pressure. Allowing such runs to stand for longer times (overnight) did not affect the yield.

TABLE IV

EFFECT OF TIME OF REACTION ON YIELD OF 1-HEXYNE

TIME (IN MINUTES)	% YIELD
10	6.7
20	14.3
30	24.1
60	32.8
120	37.8
180	37.0
1440	15.7

Stirring.—At atmospheric pressure vigorous stirring was essential to good results. The more nearly homogeneous the reaction mixture the higher the yield of alkyne obtained.

In runs in the autoclave stirring greatly reduced the time of reaction. A well-stirred mixture proceeded to maximum reaction in about one-tenth the time required for an unstirred mixture. Stirring did not seem to produce any effect on the yields obtained from autoclave runs.

Use of solvents.—Several attempts were made to replace a part of the liquid ammonia with an organic solvent. In experiments at atmospheric

[12] FAVORSKII, *J. Prakt. Chem.*, [2], **37**, 531 (1888); *ibid.*, [2], **44**, 208 (1891).

[13] HURD, Private communication, Dec. 13, 1934.

pressure the use of small amounts of ether produced no effect on the yield but gave some apparent increase in the rate of reaction by causing the two phases of the reaction mixture to disperse more readily. Increasing amounts of ether decreased the yield. In a solution containing 50 per cent. of ether and 50 per cent. of ammonia reaction proceeded too slowly to be practical.

The addition of 15 per cent. of dichlorodiethyl ether to the ammonia lowered the yield of alkyne by one-third. This substance also caused the formation during hydrolysis of emulsions which were difficult to break.

Addition of anhydrous ethylenediamine destroyed the sodium acetylide, presumably by the formation of sodium ethylenediamine with evolution of acetylene.

Addition of various materials.—In the synthesis of 1-heptyne the addition of water to the extent of 10 g. per mole of acetylide decreased the yield of alkyne by 50 per cent., while the same amount of *n*-pentanol reduced the yield by one-third.

Excess alkyl bromide did not increase the yield of alkyne, and there is some evidence that large excesses decrease the yield slightly. Large excesses of sodium acetylide lowered the yield slightly. The addition of sodium bromide in amounts above 1 mole per mole of sodium acetylide decreased the yield of alkyne somewhat, probably due to its effect in decreasing the solubility of sodium acetylide in ammonia and its salting-out action on the alkyl halide. Initial concentrations of sodium bromide similar to those resulting from the reaction of the alkyl bromide and the acetylide had no effect on the yield of alkyne.

The addition of calcium chloride to the extent of 0.5 mole per mole of acetylide did not affect the yield of alkyne. It was, however, necessary to increase the amount of ammonia when the salt was used, because of its ammonation.

With a given acetylide and halide various metals appear to have no influence on the reaction, for it has been carried out in vessels of glass, cadmium, aluminum, and iron, both rusty and bright, without any apparent difference. Likewise, stirrers of Monel metal, nickel, brass, and glass produced no discernible effects.

Alkyl halides as impurities in 1-alkynes.—The higher alkynes prepared by this reaction from alkyl bromides and chlorides were always contaminated with unreacted halide which we have been unable to remove completely by distillation, even through highly efficient fractionating columns. This contamination is most serious with chlorides because of the closeness of their boiling points to those of the corresponding 1-alkynes and because of their lower reactivity with ammonia and sodium acetylide. The amount of alkyl halide in the 1-alkyne is usually between 0.5 and 1 per

cent. with bromides, and 5 and 20 per cent. for chlorides. The use of a large excess of sodium acetylide did not have much effect in reducing the unreacted halide but some improvement resulted from thorough stirring of the reaction mixture.

A number of attempts were made to remove this alkyl halide by chemical means. Refluxing with pyridine or with magnesium for from 2 to 5 hours failed to eliminate the halides. Refluxing for 6 hours with aniline in the presence of *p*-toluenesulfonic acid and anthranilic acid had no effect on the chlorides but caused a material decrease in bromides. Refluxing for 5 hours with an excess of 50 per cent. alcoholic potassium hydroxide was effective, giving an 85 to 90 per cent. reduction in bromide content. Alcoholic sodium hydroxide is not as good as the potassium compound but does give some reduction of both bromides and chlorides. This method, however, is open to some objection, as rearrangement may take place during the treatment.[12] Treatment with sufficient sodamide in liquid ammonia to convert the alkyne to alkynylsodium and the alkyl halide to alkene and alkylamines gave a product containing only a trace of halide. Sodium metal in ammonia destroyed all of the alkyl halide but the alkynes recovered from this treatment were contaminated with alkenes.[24]

This presence of unreacted alkyl halide was found to be the most objectionable feature of the method as a source of *pure* alkynes because halide impurities were found to be the most difficult of any to remove from the finished product. For most purposes, fortunately, the presence of small amounts of alkyl halide in the alkyne is of no consequence. Because of this no persistent effort was made to overcome this difficulty.

SIDE REACTIONS

As has been previously stated, in the course of this work, several commonly occurring by-products, which appear to have been overlooked by other workers, were separated and identified. A number of attempts were also made to prevent or control the formation of these by-products which consist principally of alkenes, alkylamines, acetylene, dialkyl ethers, and dialkylethynes.

Alkenes.—It has been known since 1919 that secondary and tertiary alkyl halides,[14] as well as primary alkyl halides having a side chain on either of the two adjacent carbon atoms,[15] give only traces of 1-alkynes with sodium acetylide, but are dehydrohalogenated, giving alkenes:

$$H_3C-CHXR + NaC{\equiv}CH \rightarrow CH_2{=}CHR + NaX + C_2H_2$$
$$RR'HC-CH_2X + NaC{\equiv}CH \rightarrow RR'C{=}CH_2 + NaX + C_2H_2.$$

[14] PICON, *Compt. rend.*, **168**, 825 (1919).
[15] PICON, *ibid.*, **168**, 894 (1919).

It has not been previously pointed out, and has in fact been denied,[16] that straight-chain primary alkyl halides may react in this way. It has been our experience that the halides higher than ethyl gave a considerable proportion of 1-alkene by this method:

$$RCH_2-CH_2X + NaC\equiv CH \rightarrow RCH=CH_2 + NaX + C_2H_2.$$

Amyl bromide, for example, often gave yields of as much as 8 per cent., and occasionally 20 per cent., of an amylene which was shown by reactions as well as physical properties to be 1-pentene. Similar yields of other alkenes were also sometimes obtained. Cyclohexyl bromide reacted as a secondary halide, giving no alkyne and moderate yields of cyclohexene. Dimethyl and diethyl sulfates gave only very small amounts of ethylene, less than 0.5 per cent. being found.

It should be noted that saturated solutions containing undissolved sodium acetylide were used in most of this work. In a few cases where calcium acetylide was employed the production of alkene appeared to be diminished. From this point of view the reactions of more dilute solutions of sodium acetylide and of other less soluble acetylides should be investigated in the future.

The proportion of alkene appeared to be somewhat characteristic for each alkyl halide, but no exact correlation has been found as yet between the physical conditions of experiment and the varying yields of alkenes. The alkenes may also have resulted in part from the reaction of alkyl halides with sodamide, sodium hydroxide, or sodium alcoholates which were sometimes present.

Amines.—It has been reported[17] that the lower alkyl halides react with liquid ammonia, yielding mixtures of primary, secondary and tertiary alkylamines, and tetraalkylammonium halides. We have found that the higher alkyl halides react in similar fashion, and that in the presence of sodium acetylide this reaction is competitive with the reaction yielding the alkynes. The alkyl iodides reacted most rapidly with ammonia, with the bromides and chlorides following in decreasing order. Temperature appeared to be an important factor in controlling the rapidity of amine formation. At $-34°$ and atmospheric pressure, the reaction between ammonia and butyl bromide, for example, was rather slow, but at $-18°$ and two atmospheres pressure it was 91 per cent. complete in 3 hours, while at ten atmospheres, due to conservation of the heat of reaction in the autoclave, it was practically complete in 1 hour. Accordingly in the preparation of alkynes from alkyl chlorides or bromides at temperatures slightly above $-34°$ this side reaction causes little loss, but at 25° it may account

[16] PICON, *ibid.*, **169**, 32 (1919).

[17] PICON, *Bull. soc. chim.*, [4], **35**, 979 (1924).

for 10 to 15 per cent. of the alkyl bromide used. If it was desired to conserve the alkyl halide the use of the autoclave was, therefore, less advantageous than reaction at lower temperatures and pressures. On the other hand, if it was desired to eliminate as amine practically all of the alkyl halide not consumed in the principal reaction, the use of the autoclave with stirring gave the most satisfactory results.

Some amines may possibly have resulted from the reaction of alkyl halides with sodamide[17] which, as previously mentioned, may have existed in a small proportion in equilibrium with sodium acetylide in liquid ammonia solution,

$$NaC{\equiv}CH + NH_3 \rightleftharpoons NaNH_2 + C_2H_2$$

or which may have been formed from sodium and ammonia as previously mentioned.

In order to remove the amines from the alkynes and other products, the crude upper layer obtained from the reaction mixture was washed with dilute hydrochloric acid until acid, and then with water to remove the amine hydrochlorides which are somewhat soluble in the crude product. The omission of the washing with water led to the contamination of the distilled product with amine hydrochlorides, which dissociate during distillation and are re-formed on condensation.

Isolation of alkylamines.—The acid and water washes obtained in the treatment of crude alkynes were combined and treated with an excess of solid sodium hydroxide. The upper layer which separated was removed, dried over solid potassium hydroxide and distilled, cuts being made at points appropriate for the amines being collected. In this manner yields of butyl- and amylamines varying from 2 to 15 per cent. were obtained from various alkyne runs.

The amines obtained as by-products usually consisted of about equal proportions of the mono- and dialkylamines with variable quantities of the trialkyl compounds.

Acetylene.—The ammonium halide or sulfate formed in the ammonolysis of the alkyl esters to amines would be expected to react as an acid in liquid ammonia, and attack the sodium acetylide, with the liberation of acetylene.

$$NaC{\equiv}CH + NH_4X \rightarrow C_2H_2 + NH_3 + NaX$$

Maas and Russell[4] have claimed that propyne prepared from sodium acetylide and methyl iodide in liquid ammonia does not give a positive test for acetylene by the procedure developed by Berthelot,[18] while Tchao,[4d] states that 1-butyne prepared by this method contains small amounts of acetylene.

[18] BERTHELOT, *Ann. chim. phys.*, [4], **9**, 423 (1866).

It has been our experience that acetylene is practically always one of the products obtained in this reaction. While we have made no effort to measure the extent of acetylene formation with any accuracy, considerable quantities are formed. It will be recalled that in the experiment detailing the preparation of propyne 17 per cent. of the crude reaction product was acetylene.

In one preparation of 1-hexyne in the autoclave at room temperature, employing 5 moles of butyl bromide and other reactants, 2.5 liters of acetylene was contained in the gas evolved on releasing the pressure. This corresponds to a yield of 2 per cent. of the theoretical, assuming that all the alkyl halide reacts to form ammonium halide which in turn reacts completely with sodium acetylide. Since acetylene is very soluble in liquid ammonia, it is obvious that a still larger amount of this substance remained in solution and that the yield was actually much higher.

The removal of acetylene from alkynes causes no difficulty, as mere fractionation suffices in every instance to give good separation.

Ethers.—Unless extraordinary precautions are taken to exclude water, alcohols, and sodium hydroxide from the starting materials in this synthesis, ethers are always among the products of the reaction of alkyl halides and sodium acetylide in liquid ammonia. We have recently shown[19] that alcoholates and alkyl halides interact in liquid ammonia to give ethers by the well-known Williamson reaction. These ethers result from a series of reactions that may be represented by the scheme,

$$H_2O \xrightarrow{HC_2Na} NaOH \xrightarrow{RX} ROH \xrightarrow{HC_2Na} RONa \xrightarrow{RX} ROR.$$

The quantities of ether obtained are obviously dependent upon the amounts of water and other hydroxylic impurities present in the starting materials. With the usual precautions to exclude these compounds, yields of dialkyl ether of the order of 1 to 5 per cent. are ordinarily obtained. The ethers may be readily isolated in a pure condition by the fractionation of the residues from the distillation of the crude alkynes.

Alcohols.—As would be expected, ether formation is not always entirely complete, and an excess of alcoholate generally remains at the end of the reaction. This alcoholate upon hydrolysis, of course, gives the corresponding alcohol. We have in several instances actually isolated small amounts of amyl alcohol from residues from the distillation of 1-heptyne. The amount of this material usually represents less than 1 per cent. of the alkyl halide taken, although at times it reached 10 per cent. Because of the depressing action of alcohols on the yields of alkynes even these small amounts of alcohols may be of importance.

[19] VAUGHN, VOGT, AND NIEUWLAND, *J. Am. Chem. Soc.*, **57**, 510 (1935).

Dialkylethynes.—Some dialkylethyne nearly always resulted from the action of sodium acetylide with an alkyl halide in liquid ammonia. Butyl and amyl bromides for example, usually yielded 2.4 to 2.7 per cent of dialkylethyne, although on one occasion 30 per cent. was obtained.

Dialkylethynes have been reported[20] previously among the products of the action of alkyl halides on the Grignard reagent derived from acetylene. This reagent has been considered to be a mixture of the compounds HC≡CMgX and XMgC≡CMgX, in a proportion dependent on the conditions of experiment, and the percentage of dialkylethyne produced from from it has been looked upon as being a measure of the quantity of XMgC≡CMgX present.[21]

Previous work[8] as well as our own results indicate that the sodium acetylide prepared in liquid ammonia was substantially free from sodium carbide, Na—C≡C—Na. Enough could scarcely have been present to account for the yields of dialkylethynes obtained. It was concluded that the following series of reactions was largely responsible for the production of dialkylethynes:

(1) $RX + MC{\equiv}CH \rightarrow RC{\equiv}CH + MX$;
(2) $RC{\equiv}CH + MC{\equiv}CH \rightleftarrows RC{\equiv}CM + C_2H_2$;
(3) $RC{\equiv}CM + RX \rightarrow RC{\equiv}CR + MX$.

Reactions of type (3) have been reported by others,[4c, 4d, 27, 28] and confirmed by us in the course of the present work. The existence of reactions of type (2) was proved by treating a solution of potassium acetylide in liquid ammonia with a number of monosubstituted ethynes and noting the instantaneous precipitation of the corresponding potassium salt. Thus, with 1-heptyne a precipitate of heptynylpotassium was obtained, which, after filtration and washing with liquid ammonia, was hydrolyzed. The recovered 1-heptyne was identified from the melting point of its mercury derivative.[22] Only scanty precipitates of the apparently more soluble sodium compounds were observed, but in this case equilibrium between the ions $(C{\equiv}CH)^-$ and $(C{\equiv}CR)^-$ and the corresponding 1-alkynes probably existed in solution.

The dialkylethynes obtained from the acetylenic Grignard reagent possibly may be accounted for by a similar set of reactions (particularly in view of the fact that pure XMgC≡CMgX has been shown not to react with alkyl halides[23]). It follows also that the proportion of mono- and dimetallic acetylides in any mixture such as the acetylenic Grignard

[20] GRIGNARD, LAPAYRE, AND FAKI, *Compt. rend.*, **187**, 517 (1928).
[21] FAKI, *Contrib. Inst. Chem. Natl. Peiping*, **1**, 127 (1934).
[22] JOHNSON AND MCEWEN, *J. Am. Chem. Soc.*, **48**, 469 (1926).
[23] VAUGHN AND NIEUWLAND, to be published.

reagent cannot be safely estimated from the proportion of the derived mono- and disubstituted ethynes.

Among the factors that should influence the yield of dialkylethynes from the proposed mechanism, there was considered the proportions of acetylene and alkyne in solution, the comparative solubility and ionization of their metal salts, and the quantity of solvent ammonia. The most obvious method of decreasing the by-production of dialkylethynes is the use of excess acetylene in solution, and conversely, continuous removal of acetylene during reaction should give increased yields of dialkylethynes. Further experiments along these lines will be attempted.

The properties of the disubstituted ethynes that we have isolated from the residues from the distillation of crude 1-alkynes are listed in Table V.

Other impurities.—Besides the by-products discussed above, small quantities of other substances were sometimes present. Among these

TABLE V

PROPERTIES OF DIALKYLETHYNES

ALKYNE	B.P., °C.	d_{25}	n_D^{25}	MR_D	
				Found	Calc'd
4-Octyne	130.4–130.6/745 mm.	0.7484	1.4226	37.4	37.2
5-Decyne	105.2–105.8/ 79 mm. 172/745 mm.	0.7692	1.4311	46.5	46.4
6-Dodecyne	97.0–98.0/16 mm. 209/745 mm.	0.7753[a]	1.4351[a]	55.9	55.6

[a] At 30°.

were probably dimethylethynylcarbinol and other condensation products arising from the acetone present in Prest-O-Lite acetylene. In view of the isomerization of alkynes with both sodamide and sodium hydroxide, it seems quite possible that the shift of hydrogen atoms along the carbon chain under the influence of sodium acetylide or other alkalies may have been responsible for small quantities of by-products. Traces of sodium peroxide resulting from the action of the air on sodium solutions may have produced by-products by the oxidation or polymerization of the alkynes. The distillation of the higher-boiling alkynes usually caused polymerization of a small fraction of the material.

RELATIVE REACTIVITY OF VARIOUS ACETYLIDES

The relative order of activity of potassium, sodium, calcium and barium acetylides with respect to alkyl halides in liquid ammonia was determined.[29] Separate runs with each acetylide were made in the same

autoclave, all variables being held constant so far as possible. The rate of pressure increase in each of these experiments was measured and plotted. It was found that the slopes of the various curves were, within the limits of error, equal. There was, however, some difference in the time required for initiation of reaction. This indicates that different temperatures are necessary to initiate the reaction with various acetylides. The order of reactivity as indicated by this lag in reaction is, in decreasing order, potassium, sodium, calcium, and barium acetylide. The data on barium acetylide are not as accurate as might be desired in view of the difficulty of obtaining pure barium acetylide. The yields of alkynes obtained in these experiments are shown in Table VI.

With all these acetylides, the side reactions previously mentioned take place. No accurate data as to the extent of these side reactions and their dependence on the character of the acetylide used, were collected.

TABLE VI

YIELDS WITH METAL ACETYLIDES

ACETYLIDE	% OF 1-HEPTYNE	% OF 6-DODECYNE
Potassium	54	—
Sodium	50	—
Barium	41	—
Calcium	31	7

PREPARATION OF SODIUM ALKYNYLIDES IN LIQUID AMMONIA

Several workers[24] have reported that 1-alkynes are hydrogenated by sodium in ammonia, simultaneously with the formation of the sodium derivative. Picon[25] has advocated the use of sodamide in the preparation of alkynylides to avoid these hydrogenation losses. Work in these laboratories has shown that sodium in ammonia does hydrogenate 1-alkynes, but not to the extent previously reported. The losses, however, are serious enough to justify the use of sodamide, which in ammonia solution has lately been made available.[9] The conversion of amide to alkynylide is rapid and complete at atmospheric pressure.

PREPARATION OF DIALKYLETHYNES

Although it has been known for a number of years that sodium alkynylides can be alkylated by methyl sulfate in ether with the production of

[24] MOISSAN, *Compt. rend.*, **127**, 911 (1898); LEBEAU AND PICON, *ibid.*, **157**, 137, 223 (1913).

[25] PICON, *ibid.*, **173**, 155 (1921); *Bull. soc. chim.*, **29**, 709 (1921).

very good yields of dialkylethynes,[26] it is only recently[4c, 27, 4d] that attempts have been made to carry out this reaction in liquid ammonia. Heisig,[4c] and Heisig and Davis[28] have reported that propynylsodium can be alkylated by either methyl iodide or dimethyl sulfate, a yield of 36 per cent of 2-butyne being obtained from the iodide. We have prepared a

TABLE VII

YIELDS OF DIALKYLETHYNES

METALLIC COMPOUND	ALKYL COMPOUND	YIELD ± 5%
PrC≡CNa	PrBr	45[a]
BuC≡CNa	MeI	38[b]
BuC≡CNa	EtCl	17[b]
BuC≡CNa	Et_2SO_4	29[b]
BuC≡CNa	PrBr	45[b]
BuC≡CNa	BuBr	54[a]
AmC≡CNa	MeI	36[b]
AmC≡CNa	Me_2SO_4	17[b]
AmC≡CNa	Et_2SO_4	23[b]
AmC≡CNa	EtCl	24[b]
AmC≡CNa	EtBr	54[b]
AmC≡CNa	PrBr	42[a]
AmC≡CNa	AmCl	56[a]
AmC≡CNa	AmBr	58[a]
PhC≡CNa	MeI	43[b]

[a] Reaction conducted in autoclave and allowed to come to room temperature.
[b] Reaction conducted at atmospheric pressure.

TABLE VIII

PHYSICAL PROPERTIES OF DIALKYLETHYNES

ALKYNE	B.P. AT 750 MM.	n_D^{25}	d_{25}
BuC≡CMe	107-111°	1.4220	0.745
BuC≡CEt	127-130	1.4273	0.763
BuC≡CPr	150-154	1.4296	0.757
AmC≡CMe	131-135	1.4285	0.761
AmC≡CEt	150-154	1.4300	0.762

unmber of dialkylethynes by this reaction, the sodium alkynylides being prepared from the alkynes and sodamide in liquid ammonia. Various halides and sulfates have been used. Data on yields are included in Table VII.

[26] BOURGUEL, *Ann. chim.*, [10], **3**, 191 (1925); *Compt. rend.*, **179**, 686 (1934).
[27] JACOBSON AND CAROTHERS, *J. Am. Chem. Soc.*, **55**, 1622 (1933).
[28] HEISIG AND DAVIS, *ibid.*, **57**, 339 (1935).

It will be seen that with the lower alkyl esters good yields were not generally obtained at atmospheric pressure. With the higher alkyl esters, however, and the use of an autoclave, moderate yields were produced. These yields, however, are not so good as those claimed by Bourguel for the reaction when conducted in ether.

The nature of the alkyl group in the alkyne did not seem to influence the yield of the product to any great extent. The negative group of the alkylating agent did seem to influence the yield of the product. Alkyl bromides were the most effective reagents for this reaction, the iodides, sulfates and chlorides following in the order named.

The physical properties of the dialkylethynes not listed in Table V have been collected in Table VIII.

EXPERIMENTAL

Since the preparation of dialkylethynes at atmospheric pressure has been described elsewhere,[4c, 27, 28, 9] only the procedure used in preparing these compounds in the autoclave will be described.

Preparation of 6-dodecyne.—A solution of 125 g. of sodium in 2 liters of liquid ammonia contained in a 10-liter steel autoclave was treated with 2 g. of ferric nitrate and 1 g. of sodium peroxide. A rapid reaction set in, and in 50 minutes the sodium metal was completely converted to sodamide. 1-Heptyne (480 g.) containing as an impurity 6% of amyl chloride was dropped into this well-stirred solution during 45 minutes, a liter of ammonia being added during the same time in order to increase slightly the volume of the solution and maintain it in a fluid condition. Amyl chloride (432 g.) was added to the suspension of heptynylsodium, and the autoclave was closed. After stirring for 1 hour, at which time the pressure had reached 160 p.s.i., the reaction mixture was allowed to stand overnight. The autoclave was opened, and the reaction mixture was hydrolyzed with 2 liters of water. The large oily layer that separated was removed, washed with 1:3 hydrochloric acid and then twice with water. It was then dried over calcium chloride and distilled through an efficient column. The fractions collected were as follows:

(1)	33–95°	6 g.
(2)	95–105°	97 g.
(3)	105–115°	67 g.
(4)	115–100° at 15 mm.	18 g.
(5)	100° at 15 mm.	460 g.
(6)	residue	16 g.

The over-all yield of 6-dodecyne corresponds to 59% of the theoretical. Analysis of fraction 2 indicated that 60 g. of 1-heptyne was recovered, thus giving a net yield of 6-dodecyne of 68%. The side reactions previously mentioned all take place, but contamination of the dodecyne with alkyl halide is not a serious problem because of the wide difference in boiling points.

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CONCLUSION

The well-known reaction of metal alkynylides with alkyl halides and sulfates in liquid ammonia has been studied over a wide variety of conditions and has been applied to the synthesis of a large number of mono- and dialkylethynes. The principal disadvantage of this method for preparing 1-alkynes lies in the presence of small amounts of alkyl halides in the product. A new and rapid method for the preparation of metal alkynylides has been developed. The relative reactivities of potassium, sodium, barium, and calcium acetylides to alkyl chlorides, bromides, iodides and sulfates have been studied. A number of by-products, overlooked by other workers in the field, have been isolated and identified.

[29] SARTORETTO, M. S. Thesis, University of Notre Dame, 1934.
[30] TOBIN AND GEERTS, B. S. Theses, University of Notre Dame, 1936.