Sodium Acetylide. II. Reactions of Sodium Acetylide in Organic Diluents. Preparation of Monoalkyl Acetylenes[1]

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Dimethyl sulfate reacted with sodium acetylide in organic diluents such as xylene to form 80–85% yields of propyne, along with 8–20% yields of 2-butyne. One of the unusual features of this reaction is that both of the methyl groups of the dimethyl sulfate are utilized in the alkylation. A mixture of xylene and dimethylformamide (35–45 volume %) was found to be an excellent medium for alkylation of sodium acetylide by alkyl bromides. n-Butyl bromide reacted with sodium acetylide to form 1-hexyne in 80% yield. Several other reaction media, such as n-butyl ether–dimethylformamide, were equally satisfactory.

Monoalkyl acetylenes (1-alkynes) usually are prepared by reaction of sodium acetylide with alkyl halides, sulfates, etc., in liquid ammonia. An excellent review has been prepared by Nieuwland.[3] Vaughn, Hennion, Vogt, and Nieuwland[4] have reported results of extensive investigations of the reaction of alkali acetylides with organic halides and sulfates in ammonia. Dimethyl sulfate and diethyl sulfate reacted to form the corresponding 1-alkynes in 50–100% conversions. Only one alkyl group reacted. Alkyl bromides, from n-propyl to n-amyl, formed 1-alkynes in 44–80% yields. The higher yields were obtained at elevated temperatures and at superatmospheric pressure, an operation described as hazardous by these authors[4]. Pressure reactions were necessary for alkyl halides of 10 carbon and greater chain length. Presumably the higher temperatures achieved in this way increased the solubility of the alkyl halides, thus allowing reasonably satisfactory reaction. Alkyl iodides were too reactive, forming large quantities of by-product olefins and amines. Alkyl chlorides were less reactive than bromides. Chlorides were inconvenient because their boiling points are usually very close to those of the product 1-alkyne, making separation and purification very difficult.

When these authors[4] attempted to dilute the ammonia with organic materials, such as diethyl ether, ethylene diamine, etc., yields of 1-alkynes were greatly reduced.

In a more recent paper, Pomerantz et al.,[5] re-

ported larger scale (60 mole) preparations of various 1-alkynes. Their results confirm those reported earlier.[3,4]

Only one reference[6] was found which describes reaction of sodium acetylide with an alkyl sulfate in an organic diluent. Diethyl sulfate reacted with sodium acetylide in diphenyl ether at 190° to form 1-butyne in about 35% yield, based upon one ethyl group reacting.

The availability in our laboratories of pure finely divided sodium acetylide[1] was the starting point for the work reported here. Since the sodium acetylide was prepared in diluents such as xylene, it was decided to study these organic media for alkylation of sodium acetlide. The work was directed at simple fast reactions which could be carried out at atmospheric pressure.

Reaction of sodium acetylide with alkyl sulfates. When one mole of dimethyl sulfate was added to a slurry of two moles of sodium acetylide in xylene (prepared in xylene[1]) at 90° both methyl groups

(1) Part I. Preparation of Sodium Acetylide by Reaction of Acetylene with Sodium in Organic Media, *J. Org. Chem.*, **22**, 649–652 (1957).

(2) Present address: Atlas Powder Co., Wilmington, Del. This work was carried out at The Central Research Laboratories, Air Reduction Co., Inc., Murray Hill, N. J. The reactions described in this paper are covered by issued patents assigned to Air Reduction Co., Inc. (U.S. Patent **2,848,520** and U.S. Patent **2,846,491**).

(3) J. A. Nieuwland and R. B. Vogt, *The Chemistry of Acetylene*, Reinhold Publishing Company, N. Y., 1945, pp. 74–80.
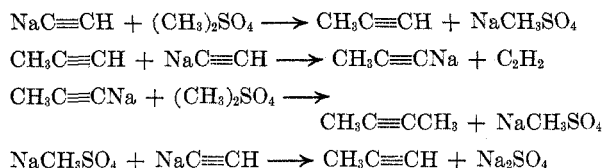
(4) T. H. Vaughn, G. F. Hennion, R. R. Vogt, and J. A. Nieuwland, *J. Org. Chem.*, **2**, 1 (1937).

(5) P. Pomerantz, A. Fookson, T. W. Mears, S. Rothberg, and F. L. Howard, *J. Res. Nat'l Bur. Standards*, **52**, 51 (1954).

TABLE I

REACTION OF SODIUM ACETYLIDE WITH DIMETHYL SULFATE IN XYLENE

	1	2	3	4
Sodium acetylide, moles[a]	0.688	0.643	0.706	1.17
Dimethyl sulfate, moles	0.344	0.321	0.353[b]	0.58[b]
Xylene, grams	165	150	173	274
Mode of addition[c]	Normal	Normal	Reverse	Reverse
Temp., °C.	90	120	90	120
Time, min.	90	90	65	58
Conversion of Acetylide, Mole %				
To propyne	85.5	73.1	82.3	83.0
To 2-butyne	7.9	17.5	11.3	10.8
Total conversion	93.4	90.6	93.6	93.8

[a] 95% pure. Conversions are based on actual sodium acetylide content.

[b] 30% excess added subsequently to complete the reaction.

[c] "Normal" addition involved addition of dimethyl sulfate to sodium acetylide slurry. In "reverse" addition, sodium acetylide slurry was added to dimethyl sulfate.

(6) O. Nicodemus, German Patent **562,010** (Feb. 20, 1931).

were observed to react. This is the first known case in which both alkyl groups of a dialkyl sulfate reacted completely with sodium acetylide. About 80–85% of the dimethyl sulfate formed propyne, and 8–10% went to 2-butyne (typical data are summarized in Table I). Total conversions were 90–95%. Addition of dimethyl sulfate at 120° resulted in less propyne, and about twice as much 2-butyne. "Reverse" addition, *i.e.*, addition of sodium acetylide slurry to dimethyl sulfate, was decidedly poorer at both temperatures. Excess dimethyl sulfate (25–30%) was required to form the same quantity of propyne, 2-butyne mixture as was obtained by "normal" addition. Again, conversion to 2-butyne was about 10%.

2-Butyne probably resulted from reaction of product propyne with unreacted sodium acetylide to form sodiopropyne (and acetylene), followed by reaction of sodiopropyne with dimethyl sulfate. Some acetylene was always found in the crude reaction products. Direct reaction of dimethyl sulfate with disodioacetylene (sodium carbide) contained in the acetylide was not possible, since disodioacetylene was never detected in the sodium acetylide.[1] Since the sodium acetylide contaned no free sodium, direct reaction of propyne to form sodiopropyne could not occur. However, in several cases sodium dispersion was added to the acetylide prior to "methylation," and increased 2-butyne formation was observed. Propyne reacted with sodium dispersion alone to form sodiopropyne under similar conditions. Thus, sodiopropyne once formed will react with dimethyl sulfate under these conditions to form 2-butyne. The necessity for a large excess of dimethyl sulfate in the "reverse" addition procedure implies that intermediate sodium methyl sulfate reacts more slowly than dimethyl sulfate, and that a small excess of sodium acetylide is necessary throughout the reaction for rapid conversion of the methyl group in sodium methyl sulfate into another mole of propyne. The following sequence of reactions is consistent with all the known facts:

$$NaC\equiv CH + (CH_3)_2SO_4 \longrightarrow CH_3C\equiv CH + NaCH_3SO_4$$

$$CH_3C\equiv CH + NaC\equiv CH \longrightarrow CH_3C\equiv CNa + C_2H_2$$

$$CH_3C\equiv CNa + (CH_3)_2SO_4 \longrightarrow$$
$$\qquad\qquad\qquad CH_3C\equiv CCH_3 + NaCH_3SO_4$$

$$NaCH_3SO_4 + NaC\equiv CH \longrightarrow CH_3C\equiv CH + Na_2SO_4$$

When diethyl sulfate was treated with sodium acetylide as described above, 1-butyne was formed in 70% yield, based on both ethyl groups reacting. This represents an average of 1.4 ethyl groups reacting per mole of diethyl sulfate. Prolonged reaction times did not increase the yield of 1-butyne.

In one experiment the sodium acetylide was prepared by the conventional liquid ammonia procedure.[4] The ammonia was replaced by xylene, and methylation was conducted at 90° in the usual manner. Yield of propyne was only 50%. This was presumably due to the fact that the sodium acetylide from liquid ammonia could not be dispersed to any

extent in the xylene. The solid remained coarse, hard, and flaky even after vigorous stirring. Hennion and Bell[7] have reported a similar experience.

Reaction of sodium acetylide with alkyl halides. Alkyl halides, such as *n*-butyl bromide, failed to alkylate our sodium acetylide in common organic diluents such as xylene, *n*-butyl ether, dioxane, and tetrahydrofuran. Consequently, a search for suitable organic diluents was undertaken. Highly polar solvents were studied first, since these alkylation reactions are ionic processes. A rapid "screening test" was devised. Sodium acetylide (dry or in xylene slurry) (0.3–0.5 gram) was placed in a few milliliters of the diluent. Two or three drops of *n*-butyl bromide were added to the slurry. After a few minutes, the characteristic odor of 1-hexyne was easily detected when suitable media were present. This simple test was used for screening dozens of diluents.

Although a number of diluents were "active" as judged by the screening test, only three diluents were found to be useful in preparative work. These were, in decreasing order of effectiveness, *N,N*-dimethylformamide, hexamethyl phosphoramide (tris-*N,N*-dimethyl phosphorus triamide), and *N,N*-dimethylacetamide. Since the best diluent (DMF) was also the most readily available and least expensive, it was studied most thoroughly. The reaction of *n*-butyl bromide with sodium acetylide to form 1-hexyne was chosen as the model. A few experiments showed that pure dimethyl formamide was not entirely satisfactory. Yields of 1-hexyne were only fair, and excessive decomposition of DMF occurred. Therefore, mixtures of DMF with other organic solvents were studied. From the data summarized in Table II (Runs 1–5), it is apparent that 35–45 volume % dimethyl formamide in xylene was quite satisfactory. This was a fortunate situation, since the sodium acetylide was usually prepared in xylene. Optimum "loading" of sodium acetylide was about 2 moles per liter of mixed diluent (Runs 8–10). Reaction time and temperature were not critical (Runs 6–7). Reaction for 4–10 hr. at 25–50° gave good yields of 1-hexyne. Best results were obtained when the butyl bromide was added to the acetylide-diluent mixture. "Reverse addition" (*i.e.*, addition of DMF to sodium acetylide and butyl bromide in xylene) resulted in lower yields. Mixtures of *n*-butyl ether and DMF were equally satisfactory.

n-Butyl chloride reacted with sodium acetylide in DMF-xylene to form 1-hexyne in only 32% yield. This parallels the yields obtained when alkyl chlorides were used in liquid ammonia.[4] *n*-Octadecyl bromide reacted with sodium acetylide in xylene-dimethyl formamide to form 1-eicosyne in 90% yield. This is superior to results obtained in liquid ammonia. No dialkyl acetylenes were found in any of the alkylation products.

(7) G. F. Hennion and E. P. Bell, *J. Am. Chem. Soc.*, 65, 1847 (1943).

TABLE II

REACTION OF N-BUTYL BROMIDE WITH SODIUM ACETYLIDE IN XYLENE-DIMETHYL FORMAMIDE MIXTURES

Run No.	1	2	3	4	5	6	7	8	9	10
Sodium acetylide, moles	0.25	0.25	0.25	0.2	0.25	0.25	0.25	1	1	1
n-Butyl bromide, moles	0.25	0.25	0.25	0.2	0.25	0.25	0.25	1	1	1
Volume, % D.M.F.[a]	25	35	44	75	92.3	91	35	37.5	37.5	37.5
Total vol. diluent, cc.	390	380	400	250	215	220	400	240	480	800
Reaction time, hr.	5	5	5	3	1	7	5	8	8	8
Reaction Temp.	25–30	25–30	25–30	30	15	−10	45–50	25–35	25–30	25–30
Product 1-Hexyne Conversion[b]	20	60	64	44	31	32.5	68	60	81	67.5
Yield[b]	66	67	71	47	31	34.5	73	60	81	67.5

[a] Dimethylformamide. [b] Mole % on butyl bromide.

All of the xylene and most of the DMF were recovered by ordinary vacuum distillation. A small amount of the DMF was lost through decomposition. The odor of dimethylamine was noticed in many crude reaction mixtures.

Increased solubility of sodium acetylide is undoubtedly at least partly responsible for the excellent results obtained in mixed diluents. Even so, sodium acetylide solubility was probably less than 0.5%. Other factors, such as solvent polarity, and solubility of any intermediates, must also be involved. More work will be required in order to explain completely the unusual "solvent" effects noted here.

EXPERIMENTAL

The procedures outlined here are typical of the many experiments conducted in the study of these alkylation reactions.

Preparation of sodium acetylide. The procedure described in Part I[1] of this series was used.

Reaction of Sodium Acetylide with Alkyl Sulfates in Xylene. A 1-liter three-necked flask was fitted with a thermometer, dropping funnel, and water jacketed reflux condenser. The exit end of the condenser was connected to two volumetrically calibrated dry ice traps. A tube of desiccant (Drierite) was placed at the end of the system to avoid condensation of atmospheric moisture in the traps.

The sodium acetylide slurry was placed in the flask, and heated rapidly to 90° (or 120°) while stirring at 600–800 r.p.m. The heat was turned off (heating mantle still in place), and dimethyl sulfate was added at a rate such that the reaction temperature was maintained at 90–95° (or 120–125°). After about 1.25 hr. the exothermic reaction ceased. The mixture was quickly heated to reflux (about 140°) until no additional material collected in traps. This usually required 5–10 min. of refluxing. The traps were then disconnected, and the total weight and volume of condensate were determined.

"Reverse" addition was identical, except that the sodium acetylide slurry was added to dimethyl sulfate heated to the desired temperature. Blank experiments showed that dimethyl sulfate was stable at these temperatures.

The composition of the crude product was determined by infrared spectrographic analysis. The instrument was calibrated with known mixtures of pure components. Composition of the crude product varied, but the product always contained a small amount of free acetylene and dimethyl ether in addition to propyne and 2-butyne. Fractionation through a low temperature column resulted in an acetylene-free propyne fraction which contained a trace of dimethyl ether, and a pure 2-butyne fraction. The dimethyl ether was removed by water scrubbing in some cases.

Reaction of sodium acetylide with n-butyl bromide in xylene-DMF mixtures. Sodium acetylide was suspended in the reaction medium (*cf.* Table II) in a 1-l. three necked flask equipped with a stirrer, dropping funnel, and water-cooled reflux condenser. The mixture was heated to reaction temperature, and n-butyl bromide was added over a period of 20 min. After the desired reaction time, the contents of the reactor were filtered (suction) into a chilled receiver. A Dry Ice trap was placed on the suction line to avoid loss of product 1-hexyne.

The filtrate was fractionated to isolate 1-hexyne (b.p. 69–71°) and unreacted n-butyl bromide (b.p. 100–102°). Total distilled 1-hexyne was confirmed in many cases by analysis.[8] Further distillation at reduced pressure was used to recover xylene and DMF. No 5-decyne was found in any of these fractions.

(8) J. G. Hanna and S. Siggia, *Anal. Chem.*, **21**, 1469 (1949).