100° at 1 mm. A picrate melting at 90.5–92.5° was prepared from the distillate. The literature[14] reports the picrate of 1,4-diethylnaphthalene to melt at 91–93°.

The material believed to be 1,1,4-triethyltetralin boiled at 174° at 50 mm; n^{20}_{D} 1.5236.

Anal. Calcd. for $C_{16}H_{24}$: C, 88.89; H, 11.11. Found: C, 88.9; H, 11.2.

Acknowledgment. The authors wish to express their appreciation to Dr. Waldo B. Ligett for his helpful suggestions and continued interest during the course of this work.

DETROIT 20, MICH.

---

[14] Arnold and Barnes, *J. Am. Chem. Soc.*, **66**, 960 (1944).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, AIR REDUCTION CO., INC.]

Sodium Acetylide. I. Preparation of Sodium Acetylide by Reaction of Acetylene with Sodium in Organic Media

T. F. RUTLEDGE

Received December 5, 1956

A procedure for preparing sodium acetylide in organic diluents is described. Sodium metal, as a dispersion, is reacted with acetylene at atmospheric pressure and at a critical temperature. Acetylene purity is extremely important. Dry, stable, finely divided sodium acetylide is described.

The preparation of sodium acetylide in liquid ammonia is a well-known reaction.[1] Liquid ammonia is relatively difficult to handle, and accordingly it has not been used extensively for large scale work. Although a fairly pure sodium acetylide can be prepared in liquid ammonia, attempts to isolate dry sodium acetylide from this reaction medium have been reported to be somewhat hazardous.[2] Experience in this laboratory confirmed a literature report[3] that sodium acetylide prepared in liquid ammonia could not be placed in inert organic diluents to form a finely divided suspension. A coarse, dark, and somewhat hard solid resulted in most cases.

Sodio derivatives of monosubstituted acetylenes are prepared readily in organic diluents such as benzene and ether.[4,5] Acetylene reacts with sodium metal in organic diluents with great difficulty. One of the few references found is a German patent[6] which describes preparation of sodium acetylide by passing acetylene into a stirred mixture of sodium and xylene at reflux temperature (about 135–140°). The product was stated to be a yellowish-white powder, the sodium acetylide content of which corresponded to 83% yield. Although no reaction time was mentioned, a time of more than 60 hours was apparently required. This is inferred from a statement contained in a later German patent,[7] which claims faster production of sodium acetylide by reaction of acetylene with sodium deposited on sand. It is interesting to note that in 1897 Matignon[8] described a process for preparing sodium acetylide which is almost identical to that described in the patent.[7]

Since sodium acetylide is an important intermediate in the practice of acetylene chemistry, it appeared desirable to find a method for fast and easy preparation of this material in organic diluents. A stable, dry powder of good purity should be valuable as a reagent.

DISCUSSION OF RESULTS

When sodium metal of 10–25 micron particle size was suspended in xylene and subsequently treated with pure acetylene at various temperatures, optimum reaction was obtained at 100–110°. The course of the reaction was followed by means of a hydrogen analyzer attached to the exit end of the reactor.[9] Complete reaction of 0.25 mole of sodium in 300 ml. of xylene required 1.5 to 2.5 hours. Yield of sodium acetylide based on sodium was virtually quantitative. Yield based on acetylene was 75–85%.

The data in Table I summarize experiments which demonstrate the effect of reaction tempera-

---

[1] T. H. Vaughn, U. S. Patent **2,198,236**, April 23, 1940. E. A. Bried and G. F. Hennion, *J. Am. Chem. Soc.*, **59**, 1310 (1937). T. H. Vaughn, G. F. Hennion, R. R. Vogt, and J. A. Nieuwland, *J. Org. Chem.*, **2**, 1 (1937). P. Pomerantz, A. Fookson, T. W. Mears, S. Rothberg, and F. L. Howard, *J. Res. Nat'l Bur. Standards*, **52**, 51 (1954).

[2] Private communications from J. H. Wotiz and M. S. Newman.

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

[4] J. R. Johnson, A. M. Schwartz, and T. L. Jacobs, *J. Am. Chem. Soc.*, **60**, 1882 (1938). H. Gilman and R. V. Young, *J. Org. Chem.*, **1**, 315 (1936).

[5] P. Ivitsky, *Bull. soc. chim. France*, **35**, 357 (1924).

[6] O. Ernst and O. Nicodemus, German Patent **494,575**, Nov. 21, 1926.

[7] W. Schulenberg, German Patent **535,071**, Feb. 8, 1929.

[8] C. Matignon, *Compt. rend.*, **124**, 775 (1897).

[9] Use of a hydrogen analyzer for this purpose was suggested by Dr. A. J. Buselli of this laboratory. This proved to be the best method of following the course of the reaction. Dr. Buselli contributed other valuable suggestions prior to and during the conduct of the work.

TABLE I

PREPARATION OF SODIUM ACETYLIDE IN ORGANIC DILUENTS (Sodium, 0.25 Moles, in 300 cc. Diluent)

Run	Diluent	Temp., °C.	Reaction Time, Hrs.	Yield[a] Sodium Acetylide (on Sodium), %
1	Xylene	100–105	2.5	99+
2	Xylene	118–120	2.75	71.5
3	Xylene	130–135	3	7.3
4	Di-*n*-butyl Carbitol	60–70	2.5	99+
5	Di-*n*-butyl Carbitol	90–100	1	99+
6	Di-*n*-butyl Carbitol	100–110	0.75	99+
7	Di-*n*-butyl Carbitol	130	3.33	59
8	Di-*n*-butyl Carbitol	145–150	1.5	49
9	Di-*n*-butyl Carbitol	160–165	3	32
10	Di-*n*-butyl Carbitol	175–180	1.25	31
11	Di-*n*-butyl Ether	75–85	2	99+
12	Di-*n*-butyl Ether	100–105	1	99+
13	Dioxane	65–70	2	99+

[a] $\text{Yield} = \frac{\text{moles sodium acetylide formed}}{\text{moles sodium consumed}} \times 100$. Sodium was consumed completely in every case.

ture on reaction time and yield. Use of several diluents is illustrated.

When xylene was the diluent (Runs 1–3) there was very striking decrease in yield of acetylide as the reaction temperature was increased from 100° to 130°. The decrease in yield was less pronounced in the case of di-*n*-butyl carbitol (Runs 4–10). In three of the diluents (Runs 4, 11, 13) excellent reactions were obtained at temperatures well below the melting point of sodium metal (97.5°). Excellent reaction occurred in dioxane at 65–70°. Attempts to prepare the pure acetylide in dioxane at temperatures below or above this range were not successful. This temperature range for dioxane was the narrowest and most critical encountered in the present work. Numerous other diluents have been utilized, optimum reaction temperature being determined as described in the Experimental Part.

Several experiments demonstrated that sodium particle size below approximately 100 microns is desirable. In two different diluents (xylene and di-*n*-butyl carbitol) use of sodium sand (about 100 microns) resulted in reaction times almost double those shown in Table I, and in yields of only about 50%.

Since commercial, or even C.P., grade sodium metal contains impurities inside the chunks or pieces, it was desirable to purify the metal before use. A simple melting procedure separated enough of the impurities to result in sodium acetylide of 98–99% purity. Unpurified sodium usually resulted in an acetylide of 95–96% purity. Sodium carbonate was the chief impurity found. When acetylene is removed from a commercial cylinder, the chief contaminant is acetone, along with trace amounts of phosphine, vinyl sulfide, arsine, and ammonia. It was found that this grade of acetylene required further purification. Acetone was a "poison" for the reaction. The trace quantities of the other contaminants were also deleterious. Numerous purification systems were investigated. Activated alumina proved to be the most efficient and convenient purification medium for laboratory work. A simple test (2,4-dinitrophenylhydrazine for acetone) was applied to the gas through the train to establish when the adsorbent required regeneration. Regeneration was accomplished by treatment with steam and/or hot air (200–300°).

Oxygen was found to be a potent "poison" for the reaction. Oxygen, particularly along with the trace impurities mentioned above, caused either very long reaction times (up to 18 hours), or no reaction at all. A maximum oxygen level of about 0.3 volume % was maintained for best reactions. This was easily accomplished, since traces of oxygen (in air) contained in commercial acetylene cylinders can be removed by "bleeding" off a few pounds of pressure from the gas phase of the cylinder. The air is reduced to a negligible amount very quickly, and the remainder of the acetylene in the cylinder can be used without difficulty. Exclusion of air from the reactor was also found to be essential.

Probably related to this effect of oxygen was the observation that sodium "dispersions" stabilized with cumene hydroperoxide failed to react with acetylene. Normal reactions could be obtained by adding hydroquinone to the dispersion before addition of acetylene. Hydroquinone did not alter the poisoning effect of oxygen, however. It was deduced from this fact that oxygen does not inhibit the reaction *via* an organic hydroperoxide.

Xylene and di-*n*-butyl ether were satisfactory as diluents after a simple drying operation. Dioxane and the polyether diluents required more careful purification (sodium or sodium hydroxide), and therefore were also distilled from sodium.

Sodium acetylide prepared in diluents such as xylene, dioxane, and butyl ether was separated as a stable, dry, palpable powder. The diluent was removed by filtration followed by pumping at 65–70° and 5 mm. pressure. Alternatively, the filtered acetylide was purged with acetylene at 100–125° for complete removal of residual diluent. It was found that the sodium acetylide adsorbed about 2.2 times its own weight of xylene, about twice its weight of butyl ether, and about 1.6 times its weight of dioxane. As expected, xylene removal was more time-consuming and difficult than was removal of butyl ether or dioxane.

The powdered acetylide, very slightly yellow to gray-white in color, was relatively stable. It could be heated to about 300° in the absence of air. Although no explosion or rapid evolution of gas occurred, the darkening of color to brown indicated probable disproportionation to sodium carbide. At 170–190° in air, a slow ignition and smooth burning occurred. At 215–235° in air, flash ignition and quiet burning was noted. The powder could be poured into a large excess of water without flashing or burning. Vigorous evolution of acetylene occurred. The material resembled powdered calcium carbide in this respect. Treatment of a large quantity of the powder with a small amount of water in the presence of air was uneventful below about 125°. Above this temperature a drop of water caused charring, glowing, and ultimately, vigorous burning of the acetylide. The acetylide was not shock sensitive. Pounding and scraping between surfaces of steel, wood, and asphalt tile in all combinations failed to cause any ignition or detonation. The storage stability of the substance was excellent. One sample was stored in the absence of air for over a year without detectable change in composition. A very slight yellowing was noted. After a year's storage, the powder was usable and reactive.

Literally hundreds of samples of sodium acetylide have been prepared in our laboratory. Many have been dried, and used subsequently in another diluent. The material resuspended quickly and easily, and suffered no loss of reactivity due to drying. The powdered acetylide prepared by this procedure was soluble in ammonia. It reacted as well as ordinary acetylide prepared in ammonia.

Examined under a microscope, the acetylide before diluent removal was in the form of spheres of the same size as the particles of sodium originally used. After diluent removal, the particles were irregular in shape, and smaller (5–15 microns) than the original sodium particles. Sodium acetylide prepared in dioxane appeared to be small spheres or circles. Numerous lines radiated from the center like spokes in a wheel. Some of the particles were small segments of a circle, half circles, etc. Here a definite crystalline form appeared probable.

Some reactions utilizing this type of sodium acetylide will be described in subsequent publications.

EXPERIMENTAL

Sodium metal (400 g.) was purified by melting under xylene in a 2 l. separatory funnel heated by means of a mantle or heating tape. The molten metal was stirred gently and the nonmetallic impurities floated to the surface of the sodium. The stopcock was then heated by means of an infrared lamp, and the sodium drained into 400 g. of dry xylene (purified or technical grade). Care was exercised to avoid nonmetallic impurities.

Preparation of sodium dispersions. Fifty wt. % "dispersions" of 10–25 micron particle size were prepared according to known methods with three different types of apparatus.[10,11] As stabilizer and dispersing agent, aluminum stearate (0.25 wt. % on sodium) and oleic acid (0.5 wt. % on sodium) were added rapidly after stirring or pumping for 3–5 minutes.

Preparation of sodium acetylide. A 1-liter, three-necked flask equipped with a crescent-blade stirrer, electric stirring motor, reflux condenser, thermometer, and a gas inlet tube (ending below the liquid surface) served as the reactor. Commercial cylinder acetylene (Airco) was passed through a stainless steel wet test meter, thence through two towers filled with 8–14 mesh activated alumina. Total weight of alumina was about 550 g. This alumina purified about 2.4 l. of acetylene per gram. Deactivation was accompanied by a yellow color in the absorbent bed, and by a positive test for acetone in the effluent gas. The exit end of the water-cooled condenser was connected *via* a trap cooled with Dry Ice to a thermal conductivity cell calibrated for direct reading of percent hydrogen in acetylene.

Xylene (300–400 ml.) was placed in the reaction vessel, and the entire apparatus flushed thoroughly with dry nitrogen to remove moisture and air. Sodium "dispersion" (0.25 mole of sodium) was added quickly, and the mixture heated to reaction temperature while stirring. Acetylene was then introduced at a rate sufficient to maintain saturation. After about 1.5 hr., the reaction mixture became gray-white (*via* a black stage), and hydrogen evolution ceased. Acetylene was then discontinued.

Isolation of dry sodium acetylide. After the reaction mixture had settled for several hours, about half the xylene was removed by decantation or pipetting. The slurry was transferred (N_2 atmosphere) into a $^1/_2$ liter, round bottom flask equipped with a plug containing a stopcock. The flask was inverted, and excess xylene filtered off through a glass wool plug or fritted glass disc. The flask was then placed upright in an oil bath held at 65–70°, and a vacuum of 5 mm. Hg applied. Pumping was continued until the dry powder reached a constant weight (usually 2–4 hours). Excessively long treatment caused some disproportionation to sodium carbide and acetylene.

Stability tests. Thermal stability was determined on an electrically heated melting point block. Samples were uncovered for access to air, and covered for determination of stability in the absence of air.

Analytical procedure. This procedure was developed by L. Barnes, Jr., L. J. Molinini, J. A. Puglisi, and Miss N. F. Hamilton of the Analytical Department of this laboratory. Their cooperation and assistance are gratefully acknowledged.

A sample (0.2–0.4 g.) was weighed into a stoppered vial in a dry-box under an atmosphere of dry nitrogen. The vial was placed in a 500 ml. suction flask, equipped with a glass tube with a stopcock on the side arm, and vacuum applied until the stopper was forced off the vial. The side arm of the flask was connected *via* a piece of glass tubing into a vessel containing 100–150 ml. of distilled water. The stopcock was opened, and the water drained into the flask. After shaking and thorough mixing (a), the alkaline solution was quickly titrated with 0.1*N* HCl to the phenolphthalein end point. (b) A few drops of methyl purple were added, and the titration continued to the end point.

$$\text{Titration (a) Free alkalinity } \frac{\text{meq.}}{\text{g.}} = \frac{\text{ml. HCl} \times N}{\text{Sample (g.)}}$$

$$\text{Titration (b) Carbonate alkalinity } \frac{\text{meq.}}{\text{g.}} = \frac{\text{ml. HCl} \times N}{\text{Sample (g.)}}$$

(c) Acetylenic hydrogen was determined as above, with a second sample of acetylide, except slaking liquid was 5% aqueous silver nitrate. A total of 100 ml. was allowed to

---

(10) Technical Promotion, Sodium Dispersions, National Distillers Chemical Company, 1953, pp. 8–9, 10–11.

(11) Stir-O-Vac unit, Labline, Inc., Chicago, Ill.

enter the flask, and the contents were shaken vigorously for 3–5 minutes. Liberated nitric acid was titrated to the methyl purple end point with 0.1N NaOH.

$$\text{Titration (c) Acidity meq./g.} = \frac{\text{ml. NaOH} \times N}{\text{Sample (g.)}}$$

$$\text{Thus: \% Sodium acetylide} = \frac{(a + b + c) \times 100}{2 \times 20.83}$$

$$\text{\% Sodium carbonate} = \frac{2b}{18.86} \times 100$$

$$\text{Free alkalinity as \% Na} = \frac{a - \left(b - \frac{a + b + c}{2}\right)}{43.48} \times 100$$

Acknowledgment. The author gratefully acknowledges the contributions of G. L. Moore, R. L. Siegmann, and T. E. Johnson, who performed a prodigious amount of experimental work, and wishes to thank B. C. Redmon, E. R. Blanchard, and A. M. Lyon for valuable suggestions and for encouragement to publish this work.

MURRAY HILL, N. J.

[CONTRIBUTION FROM THE INSTITUTE OF CHEMISTRY, FACULTY OF SCIENCES, BELGRADE, AND THE INSTITUTE OF CHEMISTRY, BELGRADE]

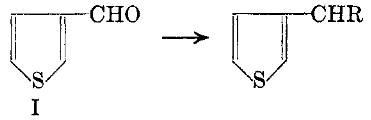
Chemistry of Thiophene. I. Derivatives of 3-Thiophenecarboxaldehyde

MIHAILO LJ. MIHAILOVIĆ[1] AND MARGITA TOT

Received November 14, 1956

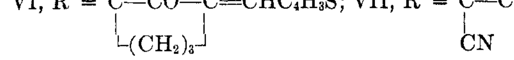
The preparation of several new derivatives of 3-thiophenecarboxaldehyde is described.

3-Thiophenecarboxaldehyde (I), which was practically unknown until 1948 when Campaigne and LeSuer[2] developed a convenient method for its preparation, starting from 3-methylthiophene through 3-thenyl bromide, so far has been studied only to a limited extent. However, many derivatives of this aldehyde might be of interest as starting products for various syntheses of 3-substituted thiophene compounds. In this paper are described the preparations of several derivatives of 3-thiophenecarboxaldehyde, which were carried out by applying some typical aromatic aldehyde condensations.

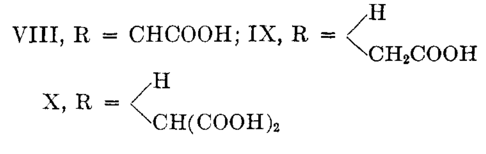


I

II, R = $(NHCOCH_3)_2$; III, R = $(NHCOC_6H_5)_2$
IV, R = NC_6H_4OH-*p*; V, R = $CHCOC_6H_5$



VI, R = $\underbrace{C—CO—C}_{(CH_2)_3}{=}CHC_4H_3S$; VII, R = $\underset{\displaystyle CN}{C}—C_6H_5$



VIII, R = $CHCOOH$; IX, R = $\left\langle\begin{matrix}H\\CH_2COOH\end{matrix}\right.$

X, R = $\left\langle\begin{matrix}H\\CH(COOH)_2\end{matrix}\right.$

3-Thiophenecarboxaldehyde (I) reacted with benzamide or acetamide in acetic anhydride to yield the corresponding well crystallized *N*,*N'*-(3-thenylidene)bisamides (II and III). Bisamides, in general, can be used for the characterization of aldehydes;[3] besides they react with most compounds containing active hydrogen atoms giving unsaturated or acylamino compounds.[4]

With *p*-aminophenol, 3-thiophenecarboxaldehyde (I) gave the corresponding Schiff base IV. In alkaline solution, I reacted with acetophenone to yield the α,β-unsaturated ketone V. The condensation of cyclohexanone with two molecules of 3-thiophenecarboxaldehyde afforded 2,6-dithenylidenecyclohexanone (VI). From I and phenylacetonitrile, in the presence of sodium methoxide, α-phenyl-β-(3-thienyl)acrylonitrile (VII) was obtained.

The Doebner modification of the Perkin reaction with malonic acid in the presence of pyridine and piperidine gave very good yields of 3-(3-thienyl)-acrylic acid (VIII). Upon reduction of VIII with sodium-amalgam, by the usual procedure, 3-(3-thienyl)propionic acid (IX) was obtained. The same acid has been previously prepared by Campaigne and McCarthy[5] from 3-thenylmalonic acid (X). If the condensation of I with malonic acid was carried out in ethanolic ammonia at 70–75°, with subsequent reduction with sodium-amalgam in the presence of carbon dioxide,[6] 3-thenylmalonic acid (X) was obtained, in 72% yield. Esterification of X with ethanol afforded the corresponding diethyl ester. Both the acid X and its ester have been previ-

---

[1] Requests for reprints should be addressed to Dr. M. Lj. Mihailović, Institute of Chemistry, Faculty of Sciences, 1, Studentski trg, Belgrade, Yugoslavia.

(2) Campaigne and LeSuer, *J. Am. Chem. Soc.*, **70**, 1555 (1948); Campaigne, Bourgeois, and McCarthy, *Org. Syntheses*, **33**, 93 (1953).

(3) Stefanović, Bojanović, and Vandjel, *Bull. soc. chim. Belgrade*, **18**, 579 (1953); Stefanović, Mihailović, Bojanović, and Vandjel, *Bull. soc. chim. Belgrade*, **20**, 417 (1955).

(4) Stefanović and Stefanović, *J. Org. Chem.*, **21**, 161 (1956). This communication contains references to previous papers about reactions of bisamides.

(5) Campaigne and McCarthy, *J. Am. Chem. Soc.*, **76**, 4466 (1954).

(6) Owen and Nord, *J. Org. Chem.*, **15**, 988 (1950).