2. The use of a co-precipitated vanadium pentoxide–aluminum oxide catalyst and super-atmospheric pressure resulted in substantial improvement in the conversion of alcohols to paraffinic hydrocarbons.

3. The general utility of the paraffinic hydrocarbon synthesis was demonstrated by successful conversion of *n*-butyl, *i*-butyl, *n*-hexyl and *n*-octyl alcohols to the corresponding hydrocarbons.

CHICAGO, ILLINOIS RECEIVED SEPTEMBER 21, 1946

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Condensation of Acetylene with Acetone and Other Ketones

BY CHARLES D. HURD AND WARREN D. MCPHEE[1]

The condensation of acetone and acetylene into dimethylethynylcarbinol dates from Merling's patents[2] in 1914, and the extension of this work by Locquin and Sung Wouseng.[3] They used sodium or sodamide as condensing agents. The method was adopted by "Organic Syntheses"[4] with a stated yield of 40–46%.

It was mentioned by Merling[2] that liquid ammonia might serve as a medium for the preparation of ethynylcarbinols, but he cited no examples making use of this procedure. McGrew and Adams[5] did use such a method in their synthesis (50% yield) of 1-pentyn-3-ol from propionaldehyde and sodium acetylide. Two patents[6] issued in 1938, employing sodamide catalyst in liquid ammonia solution, mention yields of 81–99% in the acetylene–acetone reaction. The improvement in yield, according to Kreimeier's claims, were due to the presence of a trace of hydrated ferric nitrate as catalyst during the preparation of the sodamide. Macallum used this same catalyst but specified improvement in the method of neutralization of the alkali by ammonium chloride at the end of the run. Since this time several other investigators[7] have used these procedures but yields have always been below 90%, actually 67–88%.

We are indebted to Dr. Glen H. Morey of Commercial Solvents Corporation for suggesting that traces of water in this reaction might exert an adverse effect on the yield. Experiments conducted under strictly anhydrous conditions showed that this was indeed true. Yields ranged from 86–93% when acetone was used containing no more than 0.04% water; but when 0.17% of total water was present in either the acetone or the ammonia, yields dropped to 68–75%, and when 0.54% water was present, yields were only 49–52%.

The same held for methyl ethyl ketone. The tertiary alcohol was obtained in 94% yield when an anhydrous ketone (0.003% water) was taken at the start, but only a 75% yield was obtained if 0.01% of water was present. Campbell, Campbell and Eby[8] reported yields of 60–72% for this preparation when hydrated ferric nitrate was used in the preparation of sodamide catalyst.

As might be surmised, the water of hydration in ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) was found to affect the yield of carbinol adversely, since it provided an unavoidable 0.138% of water. When used with otherwise anhydrous acetone (0.003% water), the yield of dimethylethynylcarbinol was 81%.

Experimental

Samples of anhydrous acetone (0.042 and 0.003% water) and methyl ethyl ketone (0.003% water) were kindly furnished by Commercial Solvents Corporation. Drying was effected with "Drierite" (75 g. per 500 g. of the ketone), shaking the bottles occasionally during three days.

In the experiments described below wherein anhydrous conditions were maintained, ammonia was dried with sodium and distilled directly into the reaction flask. All the glassware used was dried in an oven for three hours before use. Just before the materials were added into the reaction flask, air, dried by passage through two towers containing anhydrone, $Mg(ClO_4)_2$, was passed through the apparatus for one hour. Openings into the system were protected by tubes of anhydrone. Acetylene was dried by passage through a trap at −78° (which also condensed the acetone from the acetylene), then through the same drying towers of anhydrone which were used to dry the air. The sodium for use in the reaction was cleaned under kerosene of all oxide coating and used promptly.

Preparation of Dimethylethynylcarbinol with Anhydrous Conditions.—To 300 ml. of liquid ammonia which had been distilled into a liter 3-necked flask, cooled by Dry Ice and acetone to −50°, was added 4.6 g. (0.2 mole) of sodium in small pieces. The flask was equipped with a mercury-sealed stirrer, an inlet tube extending to the bottom of the flask, and an outlet tube. Dry acetylene was passed into the solution at the rate of 15–20 liters an hour until the blue color of sodium was discharged, leaving a suspension of white sodium acetylide. This required thirty minutes. The inlet tube was replaced by a dropping funnel containing 14.6 ml. (11.6 g. or 0.2 mole) of dry

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[1] Holder of Commercial Solvents Corporation Fellowship, 1938–1940.

[2] Merling and F. Bayer and Co., German Patents 280,226, 285,770, 286,920, 289,800, 291,185; *Chem. Zentr.*, **85**, II, 1370 (1914); **86**, II, 508, 932 (1915); **87**, I, 815, 317 (1916).

[3] Locquin and Sung Wouseng, *Compt. rend.*, **174**, 1427 (1922); *Bull. soc. chim.*, [4] **35**, 597, 604 (1924); Sung Wouseng, *Ann. chim.*, [10] **1**, 343 (1924).

[4] Coffman, "Organic Syntheses," **20**, 40 (1940).

[5] McGrew and Adams, THIS JOURNAL, **59**, 1497 (1937).

[6] Kreimeier, U. S. Patent 2,106,180 (1938); Macallum, *ibid.*, 2,125,384 (1938).

[7] Froning and Hennion, THIS JOURNAL, **62**, 653 (1940); Taylor and Shenk, *ibid.*, **63**, 2756 (1941); Hennion and Murray, *ibid.*, **64**, 1220 (1942); Backer and Blass, *Rec. trav. chim.*, **61**, 785, 924 (1942); Henne and Greenlee, THIS JOURNAL, **67**, 484 (1945); Newman, Fones and Booth, *ibid.*, **67**, 1053 (1945).

[8] Campbell, Campbell and Eby, *ibid.*, **60**, 2882 (1938).

acetone (0.042% water) which was added dropwise with stirring in one hour. The mixture, still at −50°, was stirred for four hours longer, after which time the ammonia was allowed to evaporate. The white residue was dissolved in 120 ml. of water and made slightly acidic with 50% acetic acid, 90 ml. (0.75 mole) of which were required. The clear solution that resulted was extracted six times with ether, and the combined extracts were dried with anhydrous sodium sulfate.

The ether was removed by distillation on the steam-bath. The residual liquid was distilled from an oil-bath at 145–155° through a Vigreux column, 20 × 1 cm. The dimethylethynylcarbinol, b. p. 100–102°, n^{20}_D 1.4202, weighed 14.4 g. This is a yield of 86%. There was only a small amount of solid residue and practically no forerun.

A 1-molar run was also carried out in the way described above. The procedure was identical except that the amount of ammonia (300 ml.) was not increased. Twenty-three grams (1 mole) of sodium and 73.3 ml. (56.0 g. or 1 mole) of acetone were used. The yield of dimethylethynylcarbinol, b. p. 98–105°, n^{20}_D 1.4193, was 78.1 g. or 93%.

A 0.2-molar run was made duplicating the procedures described above, except that the reagents were undried. The acetone was the technical variety. The liquid ammonia was taken directly from the tank and the apparatus was not protected from atmospheric moisture. The quantities used were 14.6 ml. (11.6 g. or 0.2 mole) of acetone, 4.6 g. of sodium and 300 ml. of liquid ammonia. Only 6.6 g. (39% yield) of dimethylethynylcarbinol, b. p. 98–103°, n^{20}_D 1.4211, was obtained.

Effect of Water on the Preparation of Dimethylethynylcarbinol.—A series of experiments was carried out in order to discover the effect that water has on the yields of dimethylethynylcarbinol. For this, the above described procedure was modified by the addition of known amounts of water to the acetone or to the liquid ammonia from a calibrated dropper. Ten drops of water from the dropper weighed 0.1455 g.; twenty drops weighed 0.2916 g. Hence one drop of water equaled 0.0146 g. The results are tabulated in Table I. The percentages of water are calculated on the weight of acetone taken, 11.6 g.

TABLE I

EFFECT OF WATER ON THE YIELD

Run	Amount of water in acetone, %	Amount of water added to ammonia g	%	Total water, %	Yield, %
1	0.042	0.0	0.0	0.042	86
2	.042	.0	.0	.042	93
3	.042	.0146	.126	.168	75
4	.042	.0292	.252	.294	68
5	.042	.0584	.504	.546	49
		Amount of water added to acetone			
1	.042	.0	.0	.042	86
2	.042	.0146	.126	.168	68
3	.042	.0292	.252	.294	58
4	.042	.0584	.504	.546	52

Use of Sodamide, Made in Liquid Ammonia with Hydrated Ferric Nitrate.—The same dry equipment was used as before. To the 300 ml. of liquid ammonia in the reaction flask was added 0.040 g. (0.0001 mole) of ferric nitrate enneahydrate $Fe(NO_3)_3 \cdot 9H_2O$. The mixture was stirred to dissolve the salt. Then 0.13 g. (0.0056 mole) of sodium was added. Dry air was bubbled through the stirred solution until the blue color changed to gray-brown. At this point 4.5 g. (making a total of 0.2 mole) of sodium was added. Nitrogen, dried the same way as the air and acetylene, was bubbled through the solution, accompanied by vigorous stirring, for nearly an hour. At the end of that time, the blue color of sodium in ammonia was lost and the mixture became gray, indicating conversion of sodium to sodamide. Dry acetylene was then passed into the reaction mixture to convert the sodamide to sodium acetylide. It was found difficult to ascertain the point of complete conversion, for there was little color change, the sodium acetylide made this way apparently being gray-black in color. However, a large excess of acetylene was used, the passage being continued up to two hours.

Dry acetone (11.6 g., 0.003% water) was added dropwise during half an hour. The stirring was continued for six hours longer, during which time a slow stream of acetylene (1–2 liters per hour) was bubbled through the mixture. The condensation reaction was brought to a close by the gradual addition of 11.8 g. (0.22 mole) of anhydrous ammonium chloride. Stirring was continued for half an hour longer, and then the ammonia was allowed to evaporate. The residue, consisting mainly of sodium chloride and dimethylethynylcarbinol, was extracted thrice with ether. The combined extracts were dried with anhydrous sodium sulfate. The ether was removed by distillation and the residual dimethylethynylcarbinol was collected between 98–105°.

The effect of water on this synthesis was investigated in the manner reported in the previous section. Known amounts of water were added to the acetone. The standard procedure, reported above, was used throughout. The results are recorded in Table II. The percentages of water are based on the weight of acetone taken, 11.6 g.

TABLE II

Run	Amount of water in acetone, %	Amount of water in $Fe(NO_3)_3 \cdot 9H_2O$ g.	%	Amount of water added to acetone g.	%	Total water, %	Yield, %
1	0.003	0.0161	0.138	0.0	0.0	0.141	81
2	.003	.0161	.138	.0146	.126	.267	56.5
3	.003	.0161	.138	.0438	.378	.519	48

Preparation of Methylethylethynylcarbinol.—The apparatus and procedure were similar to those used for dimethylethynylcarbinol. To 300 ml. of liquid ammonia at −80° was added 23 g. (1 mole) of clean, dry sodium in as large pieces as convenient. The mass was stirred and dry acetylene was passed into it until the blue color was discharged. In the course of an hour 89.5 ml. (72 g. or 1 mole) of methyl ethyl ketone (0.003% water) was added dropwise. The mixture was stirred at −80° for four hours longer while acetylene was passed into it at the rate of 1–2 liters per hour.

The ammonia was removed by evaporation and the solid white residue was taken up in a convenient amount of water (400–500 ml.). The clear solution was titrated with 50% acetic acid. Some methylethylethynylcarbinol floated on the water. It was separated and dried with drierite. The water portion was extracted six times with ether, and the combined extracts were dried with drierite. The carbinol portion was distilled at atmospheric pressure, yielding 47.2 g. of methylethylethynylcarbinol, b. p. 119–120.5°, n^{20}_D 1.4310. The ether extracts yielded 45.0 g. of the carbinol, b. p. 116–119.5°, n^{20}_D 1.4305. The total yield was, therefore, 92.2 g. or 94%.

A 0.2-molar preparation of methylethylethynylcarbinol was carried out with 0.0584 g. of water added to the 14.4 g. of dry methyl ethyl ketone. The added water increased the amount of water present from 0.003 to 0.408% by weight. The procedure and materials were the same as those described above. However, the yield of methylethylethynylcarbinol, b. p. 116.5–120.5°, n^{20}_D 1.4304, fell to 14.7 g. or 75% of the theoretical.

Preparation of *n*-Hexylmethylethynylcarbinol.—The reagents and apparatus were similar to those described above. The 2-octanone (100 g.) was treated with 150 g. of sodium bisulfite dissolved in 250 ml. of water and 63 ml. of alcohol. The mixture was shaken for four hours and a voluminous white solid formed. This was filtered off, washed several times with water and once with alcohol, and then decomposed by treatment with 150 g. of anhydrous sodium carbonate in 300 ml. of water. The mixture was steam-distilled and the 2-octanone was separated from the water in the distillate. It was dried twice with drierite and distilled. A total of 70 g. of 2-octanone was recovered (70% yield). The first 25 ml. of the ketone was discarded and the next 40 ml. was collected, b. p. 173.3–173.7°, $n^{20}\mathrm{D}$ 1.4141.

To 300 ml. of anhydrous ammonia at −80° was added 4.6 g. (0.2 mole) of clean sodium. Acetylene was passed in to form sodium acetylide. Then 31.4 ml. (25.6 g. or 0.2 mole) of 2-octanone was added rapidly (in five minutes), to prevent solidification in the stem of the dropping funnel. The mixture was stirred for four hours at −50 to −80° while a slow stream (1–2 l. per hour) of acetylene was passed in. The solid left after the ammonia had been evaporated was mixed with a liter of water. Then glacial acetic acid was added until the mixture was neutral. The solution was extracted thrice with ether and the combined extracts were shaken with two portions of sodium bisulfite solution, each composed of 40 g. of sodium bisulfite in 60 ml. of water and 25 ml. of alcohol, and after each shaking the ether solution was allowed to stand over the bisulfite solution for an hour. The ether solution was then dried with anhydrous sodium sulfate and distilled on the steam-bath. The residue was distilled under reduced pressure through a 25 × 1 cm. Vigreux column. The *n*-hexylmethylethynylcarbinol, b. p. 73–75° (7 mm.), $n^{20}\mathrm{D}$ 1.4418, weighed 18.4 g., or a yield of 60%. The main portion had a b. p. 75 ± 0.1° (7 mm.). The product gave an immediate precipitate with ammoniacal silver nitrate and none with a saturated solution of 2,4-dinitrophenylhydrazine in 10% alcoholic sulfuric acid. The b. p. at atmospheric pressure was 195–196°.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.75; H, 11.98.

Summary

Attention is called to the great spread in yields reported for dimethylethynylcarbinol as synthesized by condensation of acetone and acetylene. The present work shows the necessity for strictly anhydrous conditions if this condensation is carried out with sodamide in the presence of liquid ammonia. As little as 0.5% of water in the acetone causes a drop in yield from 90% or higher. to about 50%. Methyl ethyl ketone behaves similarly.

The synthesis of *n*-hexylmethylethynylcarbinol from 2-octanone is described.

EVANSTON, ILLINOIS RECEIVED AUGUST 8, 1946

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Reaction of Hydrogen Sulfide with Acrylonitrile, Acrylic Ester and Crotonaldehyde

BY LEON L. GERSHBEIN AND CHARLES D. HURD

Previous syntheses of β-thiodipropionic acid derivatives have usually been by way of the metathetical reaction of sodium sulfide with the corresponding β-halopropionic compounds. Examples include β-thiodipropionic acid[1] from sodium β-halopropionate, and 2-cyanoethyl sulfide[2] from β-chloropropionitrile. Sulfides result also[3] from the addition of hydrogen sulfide to compounds of the ethylene type (ethylene, styrene, acrylonitrile, *p*-divinylbenzene, vinylanisole). No basic agent was specified with acrylonitrile, the conditions merely comprising heating the nitrile with hydrogen sulfide in butanol for ten hours in a sealed vessel.

A related observation is the formation of methyl β-mercaptoisobutyrate[4] by reaction of 1.5 moles of hydrogen sulfide with one mole of methyl methacrylate at 200° under pressure. Vaughan and Rust[5] have commented on the difficult photoaddition of hydrogen sulfide to methyl methacrylate at 0°. The trace of product could be precipitated by lead or silver ions.

Published work on the behavior of hydrogen sulfide toward acrolein points to a different course of reaction, giving an oxygen-free product. Using gaseous hydrogen sulfide, Peytral[6] obtained a yellow oil and assigned to it a mercaptopropanethial structure. An alkanethial was reported also by others,[7] who dissolved acrolein in liquid hydrogen sulfide.

The present investigation was undertaken to gain added information concerning the reaction between hydrogen sulfide and acrylonitrile, acrylic esters, or crotonaldehyde, especially as regards the influence of basic catalysts and the use of simpler equipment not calling for high pressures. No reaction occurred at 25 or at 75° if acrylonitrile was merely stirred in an atmosphere of hydrogen sulfide. The introduction of small amounts of sodium methoxide or a quaternary ammonium hydroxide, however, brought about a significant change. The stirred reaction mixture now absorbed hydrogen sulfide exothermically so that external cooling was necessary. High yields of 2-cyanoethyl sulfide were obtained.

Under similar conditions methyl acrylate reacted smoothly with hydrogen sulfide to produce methyl β-thiodipropionate in excellent yield. This ester is new. Ethyl β-thiodipropionate is the only simple ester of this type previously described.[1b]

In view of these results, it was quite unexpected to find that methyl methacrylate was indifferent toward hydrogen sulfide in the presence of trimethylbenzylammonium hydroxide, even

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(1) (a) Loven, *Ber.*, **29**, 1137 (1896); (b) Bennett and Scorah, *J. Chem. Soc.*, 196 (1927).

(2) Nekrassow, *J. prakt. Chem.*, [2] **117**, 211 (1927); *J. Russ. Phys.-Chem. Soc.*, **59**, 921 (1927); *Chem. Zentr.*, **99**, I, 2926 (1928).

(3) Keyssner, U. S. Patent 2,163,176 (1939).

(4) Burke and Peters, Canadian Patent 428,507; *C. A.*, **39**, 5254 (1945).

(5) Vaughan and Rust, *J. Org. Chem.*, **7**, 475 (1942).

(6) Peytral, *Bull. soc. chim.*, [4] **29**, 41 (1921).

(7) Borgeson and Wilkinson, THIS JOURNAL, **51**, 1454 (1929).