

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_D^{20} 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_D^{20} 1.4418, weighed 18.4 g., or a yield of 60%. The main

portion had a b. p. $75 \pm 0.1^\circ$ (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.

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

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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 acid¹ from sodium β -halopropionate, and 2-cyanoethyl sulfide² from β -chloropropionitrile. Sulfides result also³ 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 -mercaptoisobutyrate⁴ by reaction of 1.5 moles of hydrogen sulfide with one mole of methyl methacrylate at 200° under pressure. Vaughan and Rust⁵ 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.

(1) (a) Loven, *Ber.*, **29**, 1137 (1896); (b) Bennett and Scourah, *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).

Using gaseous hydrogen sulfide, Peytral⁶ 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

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

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

at 80–95°. In one experiment a trace of sulfur-containing residue was obtained after removal of unreacted ester, but it was not characterized except to establish the presence of methyl methacrylate polymer and the absence of mercapto groups. This is in line with the sluggish photochemical reaction reported by Vaughan and Rust.⁵

Sodium acrylate solutions, either as such or in the presence of added alkali, did not react with hydrogen sulfide at temperatures of 25–100°. Acrylic acid was recoverable as such.

The reaction between hydrogen sulfide and crotonaldehyde was very slow at 25°, and even at 65° less than the calculated amount of hydrogen sulfide was absorbed (basic catalyst) after prolonged treatment. A distillable fraction was obtained which was very viscous. It was predominantly β -thiodibutyraldehyde as judged by boiling point and by carbon, hydrogen and sulfur analyses, but the slightly high value found for sulfur suggests the presence of a little -thial contaminant. The product contained no mercapto groups and it gave rise to no crotonaldehyde when treated with mineral acid. Evidently crotonaldehyde more nearly resembles acrylonitrile than acrolein in its reaction with hydrogen sulfide.

Experimental

Commercial grades of acrylonitrile, methyl acrylate, and methyl methacrylate were distilled before use to remove any inhibitors. The trimethylbenzylammonium hydroxide employed was 35% "Triton B" solution (Röhm and Haas). Sodium methoxide powder was the commercial product.

2-Cyanoethyl Sulfide.—Into a 3-necked flask, equipped with stirrer, thermometer and delivery tube for gaseous hydrogen sulfide, was placed 32 g. of acrylonitrile. Air in the flask was displaced by hydrogen sulfide (Kipp), then the connections were tightened, and the mixture was stirred. No hydrogen sulfide was absorbed either at 25 or 75°. Distillation led to the recovery of acrylonitrile with no higher boiling residue.

An exothermic reaction, with the temperature ascending to 72°, was caused by the presence of 0.10 g. of trimethylbenzylammonium hydroxide solution in the acrylonitrile (36.6 g. or 0.691 mole). By intermittent cooling, the temperature was held at 65–70°. More rapid absorption was favored at the higher temperatures. Reaction ceased after a 10.2-g. increase in weight had occurred. The viscous liquid product was taken up in 50 ml. of benzene, washed with dilute hydrochloric acid and water, and then dried over sodium sulfate. A fraction was obtained, b. p. 191–194° (7 mm.). Yields in several runs ranged from 41.5–45.0 g. (86–93%, based on acrylonitrile). Yields in this range were also achieved when a trace of sodium methoxide was employed as basic catalyst. Since a little air seeped into the apparatus through the sleeve of the stirrer, this was displaced occasionally by hydrogen sulfide. As this process may have caused the loss of a little of the acrylonitrile, the above yields represent minimum values. No mercaptide precipitated when the product was treated with lead acetate.

In another run the addition of hydrogen sulfide was interrupted when 6.6 g. (0.194 mole) of it was absorbed by 38.5 g. (0.726 mole) of acrylonitrile and 0.11 g. of "Triton B" solution; yield, 26.8 g. (0.191 mole). Only traces of mercapto compound occurred in a small first cut. We confirmed Nekrassow's² observation that 2-cyanoethyl sulfide could be hydrolyzed quantitatively with concentrated hydrochloric acid to β -thiodipropionic acid of m. p. 129–130°.

Methyl β -Thiodipropionate.—When hydrogen sulfide was introduced into the system containing 22.9 g. of methyl acrylate and 0.11 g. of "Triton B" solution absorption occurred at once. The temperature rose to 75° and was maintained at 65–70° by external cooling. When no more gas was absorbed, the product was processed as in the above example and distilled; yield 24.5 g. (89.4%, based on the ester) collected at 161–162° (18 mm.). On redistillation, the methyl β -thiodipropionate boiled at 148.5–149° at 8 mm., n_D^{20} 1.4750, d_4^{20} 1.156.

Anal. Calcd. for $C_8H_{14}O_4S$: C, 46.58; H, 6.84. Found: C, 46.86; H, 7.07.

Addition of Hydrogen Sulfide to Crotonaldehyde.—A rapidly stirred mixture of 27.2 g. of crotonaldehyde and 0.14 g. of "Triton B" absorbed hydrogen sulfide quite slowly at 25–40°. A small absorption (5.4 g.) occurred when the bath temperature was 60–70°. The contents became very sirupy on cooling to room temperature. Unreacted crotonaldehyde was removed at reduced pressure, then the following fractions were taken at 8–3 mm.: 6.4 g. at 82–106°, 4.7 g. at 107–135° and 5.4 g. at 135–136°. Each cut possessed a foul, non-lachrymatory odor, and each was very viscous. Each cut gave positive aldehyde tests, and a negative mercaptide test when treated with lead acetate. No breakdown into crotonaldehyde was apparent on treatment of the fractions with a few drops of sulfuric acid and warming the mixture. The sulfur content of the 107–135° fraction was 25.5%. The 135–136° fraction was analyzed for carbon, hydrogen and sulfur.

Anal. Calcd. for $C_5H_8O_2S$: C, 55.17; H, 8.05; S, 18.39. Found: C, 55.16; H, 8.41; S, 19.73.

A 2,4-dinitrophenylhydrazone of the last fraction was made by treatment with 2,4-dinitrophenylhydrazine in boiling alcohol. It was very insoluble and melted with decomposition at 219–221°. Analyses pointed to the mono hydrazone, $CHO-CH_2CH(CH_3)-S-CH(CH_3)-CH_2-CH=N-NHC_6H_3(NO_2)_2$, with some contamination by the bis hydrazone.

Anal. Calcd. for $C_{14}H_{18}N_4O_8S$: N, 15.8; S, 9.04. Calcd. for $C_{20}H_{22}N_8O_8S$: N, 21.0; S, 6.00. Found: N, 16.5; S, 8.51.

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Summary

Acrylonitrile or methyl acrylate reacts readily with hydrogen sulfide if a basic catalyst is present to form 2-cyanoethyl sulfide or methyl β -thiodipropionate, respectively. Methyl methacrylate does not undergo this type of reaction.

Crotonaldehyde, under similar conditions, reacts slowly with hydrogen sulfide yielding β -thiodibutyraldehyde as the chief product.

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