Synthesis of Mercaptoacetonitrile under Mild Conditions

By ECKART MATHIAS* and MICHAEL SHIMANSKI

(*W. R. Grace & Co., Washington Research Center,* 7379 *Route* 32, *Columbia, Maryland* 21044)

Summary Treatment of chloroacetonitrile with aqueous sodium hydrosulphide, at 0 °C or below, gives mercaptoacetonitrile in 50—53% yield.

THERE are few references to the synthesis of mercaptoacetonitrile and none of these describes its isolation or synthesis from chloroacetonitrile.[1] Mercaptoacetonitrile is a potentially useful compound for the synthesis of α-lactam intermediates and mercaptoacetic acid, and we report here its synthesis using mild conditions. Mercaptoacetonitrile is unstable and can vigorously polymerize, and/or be oxidized to the disulphide at ambient temperatures and/or under basic conditions. The mild reaction conditions described herein diminish the instability problem.

To a 35% aqueous solution of sodium hydrosulphide (0·68 mol) at −22 °C was added chloroacetonitrile (0·68 mol), at once, under nitrogen. After *ca.* 2 h, the temperature began to rise suddenly as the pH gradually decreased to 8·4 (initial pH >12). The mixture was quickly cooled to −22 °C again. When sodium chloride was seen crystallizing out, the mixture was allowed to warm to 0 °C during 1 h. Sulphuric acid was then added to bring the pH to 1, and any hydrogen sulphide generated from unchanged sodium hydrosulphide was removed *in vacuo*. The products† were extracted with methylene dichloride (3 × 50 ml). After removing the solvent *in vacuo* mercaptoacetonitrile was isolated by distillation (34 °C at 2 Torr) and then stabilized with concentrated phosphoric acid (0·5 ml).

The identity of mercaptoacetonitrile was confirmed by i.r., ^{1}H n.m.r., and ^{13}C n.m.r. spectroscopy, and by iodimetric thiol-analysis: ^{1}H n.m.r. ($CDCl_3$) δ 2·44 (1 H, t, SH) and 3·36 (2 H, d, $SCH_2C{\equiv}N$); ^{13}C n.m.r. ($CDCl_3$) δ 9·5 (CH_2) and 118·0 p.p.m. ($C{\equiv}N$); ν_{max} (liquid film) SH 2560, 920; $C{\equiv}N$ 2240; CH_2 2980, 2940, 1400 cm^{-1}.

Since the reaction is very exothermic, the temperature is best controlled by slowly stirring the mixture near its freezing point (−22 to −24 °C); high temperatures lead to low yields (Table). The method of adding the reactants can be critical, with the best yields obtained when using

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† The disulphide $N{\equiv}CCH_2{\cdot}S{\cdot}S{\cdot}CH_2C{\equiv}N$ is the major by-product.

the addition sequence described above. Slow additions and/or reverse additions of reactants (at −22 °C) led to yields below 3%.

TABLE. Effect of temperature on the yield of mercaptoacetonitrile.

Reaction time/h	Initial temp./°C	Maximum temp./°C[a]	% Yield[b]
1·1	20	105	1·2
1·1	0	40	15·0
1·7	−10	2	39·2
2·9	−22	0	50·5
3·1	−22	−15	53·4

[a] Maximum temperature observed before sodium chloride was seen crystallizing out of solution. [b] Based on iodimetric thiol-analysis.

Extreme caution should be used in handling concentrated or pure mercaptoacetonitrile. While phosphoric acid stabilizes it to some extent, sudden vigorous polymerization, with decomposition, may ensue. Gaseous decomposition products which lead to foaming of the polymerizing compound may burst the container, even when kept in a refrigerator. Nevertheless, stabilized samples of mercaptoacetonitrile have been kept for up to 3 weeks.

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[1] R. Aries, Fr. P. 2,196,645/1974; reactions of alkyl chloride and sodium hydrosulphide, E. E. Reid, 'Organic Chemistry of Bivalent Sulfur,' Vol. I, Chemical Publishing Company, Inc., New York, 1958, pp. 25—28; Union Oil Co., U.S.P. 2,816,145/1957; Hooker Electrochemical Co., U.S.P. 2,404,425/1946.