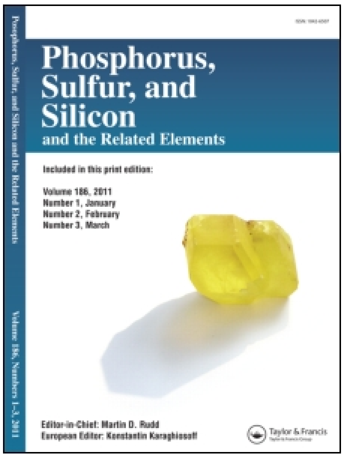

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REACTION OF ELEMENTAL SULFUR WITH ACRYLONITRILE. SYNTHESIS OF 1,7-DICYANO-3,4,5-TRITHIAHEPTANE

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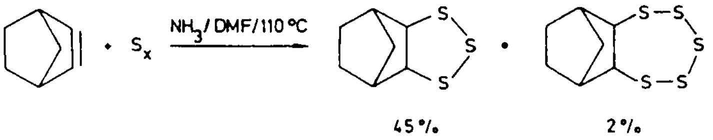
Reaction of acrylonitrile with elemental sulfur, catalysed by ammonia in dimethylformamide at 80°C results in 1,7-dicyano-3,4,5-trithiaheptane. Spectral data of this new derivative of acrylonitrile are included.

INTRODUCTION

The reaction of different forms of elemental sulfur (denoted further as S_x) with unsaturated compounds gives usually complex mixtures of products containing cyclic and linear mono- and polysulfides, thiols etc.[1–4] Only a few reactions are known, in which well defined polysulfides with relatively high yields are produced. For example, tetrafluoroethylene reacts with boiling sulfur under normal pressure (445°C) forming mainly cyclic tri- and tetrasulfides.[5,6] Norbornene and its derivatives (di-and tricyclopentadiene)[7–9] in polar solvents (dimethylformamide (DMF), dimethylsulfoxide, pyridine) in the presence of "sulfur activators" (e.g. ammonia, amines, 2,5(octyldithio)-1,3,4-thiadiazole) readily react with elemental sulfur above 100°C giving cyclic trisulfides and in considerably lower extent higher polysulfides,[4,9,10] e.g.



(1)

Similar reaction of cycloheptatriene and sulfur results in bicyclic heptatriene trisulfide.[11] In the present paper we describe the reaction of acrylonitrile (**1**) with elemental sulfur (S_x) in which, in contrast to the above quoted data, the linear trithiaderivative is formed as the major product

RESULTS AND DISCUSSION

In order to obtain polythiaderivatives of **1** we have adopted the method of Shields and Kurtz used for sulfuration of norbornene.[7] In DMF saturated with NH_3 **1** reacts easily with S_x below 100°C, giving mainly, as it will be substantiated later, 1,7-dicyano-3,4,5-trithia-heptane (**2a**):

$$\mathbf{1} + S_x \xrightarrow{NH_3/DMF/80°C} \underset{\mathbf{(2)}}{NC{-}CH_2CH_2{-}SSS{-}CH_2CH_2{-}CN} \qquad (2)$$

The structure of the product of reaction (2), i.e. **2** was established by spectroscopic (see below) and confirmed by chemical evidences. The latter were as follows:

$$NC{-}CH_2CH_2{-}Cl + K_2S_3 \xrightarrow{H_2O/80°C} \underset{\mathbf{(2)}\ 20\%\ \text{yield}}{NC{-}CH_2CH_2{-}SSS{-}CH_2CH_2{-}CN} \qquad (3)$$

$$\mathbf{2} \xrightarrow{36\%\ HCl} \underset{\mathbf{(3)}\ 90\%\ \text{yield}}{HOOC{-}CH_2CH_2{-}SSS{-}CH_2CH_2COOH} \qquad (4)$$

$$Cl{-}CH_2CH_2COONa + K_2S_3 \xrightarrow[2)\ 36\%\ HCl]{1)\ H_2O/80°C}$$

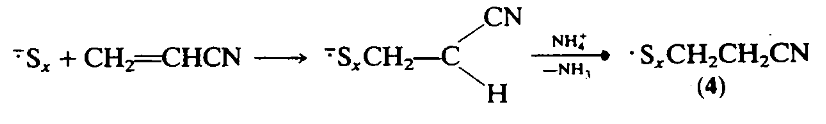
$$\underset{\mathbf{(3)}\ 56\%\ \text{yield}}{HOOC{-}CH_2CH_2{-}SSS{-}CH_2CH_2{-}COOH} \qquad (5)$$

The spectral features of **2**, the alleged 1,7-dicyano-3,4,5-trithiaheptane, were as below: IR (Jena-Zeiss UR-10, KBr pellets): 2240, 1410, 1310, 1220, 470 (ν in cm^{-1}); MS (GC MS 2091 LKB, 70 eV): 204 (M$^+$), 150, 118, 86, 54; ^{13}C-NMR (15.3 MHz, Jeol-FX 60, in CDCl$_3$, TMS internal standard): δ 15.6 (t, —CH$_2$CN, $J_{C-H} = 138$ Hz) δ 31 (tt, —CH$_2$S$_3$—, $J_{C-H} = 144$ Hz, $J_{C-CH} = 6.7$ Hz) δ 116 (m, —CN); ^{1}H-NMR (60 MHz, Perkin Elmer R12B, in CDCl$_3$, TMS internal standard): δ (3.2–3.6) (complex region indicating on A$_2$B$_2$ system, —S$_3$CH$_2$CH$_2$CN). Spectra of **2** obtained from (2) and (3) (solutions having the same weight concentrations) can be superimposed, being practically identical. Acidic derivatives of **2**, namely **3** from (2), (3) and ClCH$_2$CH$_2$—COONa gave identical IR, MS, and ^{1}H-NMR spectra. Melting points (m.p.) of **2** and **3** are in the ranges: 45–46°C and 154–156°C respectively. Additionally, after mixing equal masses of **2** from (2) and (3), and of the two specimens of **3** from reactions (4) and (5) no m.p. depression was observed. Thus, the above observations confirms our opinion, if that **2** is indeed 1,7-dicyano-3,4,5-trithiaheptane.

The mechanism of sulfurizing action of elemental sulfur-NH$_3$ system is still unknown. However it has been previously shown[12] that in polar solvents S$_8$ and NH$_3$ participates in complex equilibria. It can be suggested that during mixing of S$_8$ and NH$_3$ in DMF the following equilibrium (6) is established:

$$S_8 + 2NH_3 \rightleftharpoons NH_2S_y^{-} + S_x^{\overline{\cdot}} + NH_4^+ \qquad (6)$$

and after introduction of **1** into the resulting solution the attack of $S_x^{\overline{\cdot}}$ radical anion on the electron deficient H$_2$C═carbon atom in the vinyl group is followed by the reaction of the resulting carbanion with ammonium cation:



$$^{\overline{\cdot}}S_x + CH_2{=}CHCN \longrightarrow {}^{\overline{\cdot}}S_xCH_2{-}\overset{CN}{\underset{H}{C^{-}}} \xrightarrow[-NH_3]{NH_4^+} \underset{\mathbf{(4)}}{\cdot S_xCH_2CH_2CN} \qquad (7)$$

Radical **4** can afterwards recombine giving α,ω-dicyanoethylpolysulfide ($(NC—CH_2CH_2)_2S_x$ (**5**). Subsequent reactions of excess of radicals **4** with the polysulfide bridges $—S_x—$ in **5** (scrambling) lead eventually to a certain distribution of the number of S atoms in **5** with the predominant value of $x = 3$.

The procedure of synthesis of **2** from elemental sulfur and acrylonitrile (reaction 2) is as follows: 40.6 g (1.27 g-atom) of finely powdered S_x was stirred one half of an hour at 35°C with 500 cm^3 of DMF and NH_3 was bubbled through. Then 53 g (1 mole) of **1** was added and the resulting mixture was heated and kept at 80°C during 50 min. with vigorous stirring. When **1** was already reacted (at least 99%, by gas chromatography) the reaction mixture was quenched with ice water and afterwards extracted three times with diethyl ether. Evaporation of ether followed by recrystallization from toluene resulted in 50 g of the crude product (50% yield on acrylonitrile) which could additionally be purified by high-vacuum sublimation to white powder with m.p. 45–46°C (up to 49% yield on acrylonitrile). Elemental analysis: calculated for $C_6H_8N_2S_3$ (in wt-%): C-35.26; H-3.95; N-13.70; S-47.08, found: C-36.18; H-3.9; N-13.46; S-46.6. The spectral data of **2** are listed above. For comparison 1,7-dicyano-3,4,5-trithiaheptane was also obtained from K_2S_3 and 2-chloropropionitrile by means of the procedure similar to that described elsewhere.[13] Preparation of dicarboxylic derivatives **3** from **2** and reaction (5) were also described elsewhere (ref. 14 and 15 respectively).

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