

ADDITION OF SULFUR CHLORIDES TO THE CYANOGEN BOND IN SULFONYL CYANIDES

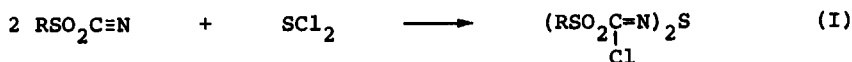
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(Received in UK 2 January 1974; accepted for publication 28 January 1974)

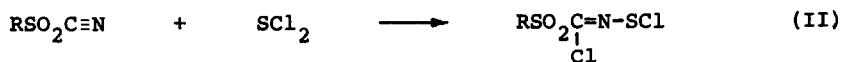
Chlorine is known to add to the activated cyano group of sulfonyl cyanides, as was reported in our previous paper¹. It now appears that sulfur dichloride and disulfur dichloride add similarly to sulfonyl cyanides, providing new interesting adducts.

In dichloromethane solution at 0°, catalyzed by tetrabutylammonium chloride, sulfur dichloride gives thiobis(-sulfonylformimidoyl chloride) (I) as an 1 : 2 adduct:

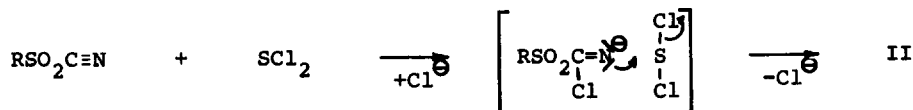


This result, recently reported by Kristinsson², prompts us to reveal further details concerning our independent investigations in this field.

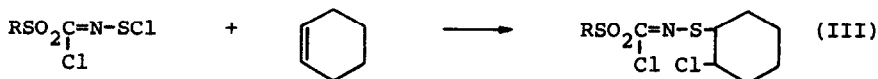
Under the same conditions, but using a 1 : 1 molar ratio of reactants, the mono-addition compound (II), a N-chlorothio-sulfonylformimidoyl chloride can be isolated or trapped.



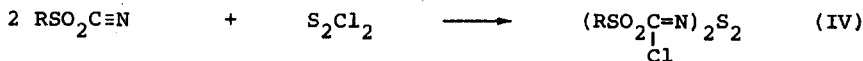
The following mechanism, accounting for chloride ion catalysis, is proposed:



When a second equivalent of the sulfonyl cyanide is present, II reacts further to give I. If not, either II crystallizes from the reaction mixture, or may be obtained by evaporating the solvent. Alternatively it can be trapped by an addition reaction to cyclohexene, to give a N-(2-chlorocyclohexylthio)-sulfonyl formimidoyl chloride (III).



When disulfur dichloride is added to benzenesulfonyl cyanide at 0° in dichloromethane as a solvent, again using tetrabutylammonium chloride as a catalyst, dithiois(benzenesulfonylformimidoyl chloride), (IVb) is formed:



An attempt to cleave the sulfur-sulfur bond in IVb (R=C₆H₅) with chlorine, in order to obtain IIB, at 70° in a Carius tube, resulted in the formation of benzenesulfonyl chloride (88%) and chlorothioimidocarbonyl chloride (72%).



We have indications that an 1 : 1 adduct of IIB with chlorine is intermediate in this reaction.

Compounds prepared: (R, yield, and melting point given)

I: a, CH₃, 91%, 211-2° dec. (ref. 2: 90%, 233°); b, CH₃CH₂CH₂, 95%, 115-6°; c: cyclo-C₆H₁₁, 94%, 117-19°; d, C₆H₅, 93%, 156-8° (ref. 2: 89%, 156°); e: p-CH₃C₆H₄, 87%, 148-9, 5° (ref. 2: 90%, 143°); f: p-CH₃OC₆H₄, 90%, 100-2°; g: p-ClC₆H₄, 93%, 175-7°; h, p-O₂NC₆H₄, 92%, 207-8°.

II: a, CH₃, 30% after distillation, which could not be effected without partial decomposition into sulfur dichloride and methanesulfonyl cyanide. Bp: 101-3°/0,5; b, C₆H₅, >64% as based on the reaction with cyclohexene; could not be purified by distillation; c, p-O₂NC₆H₄, 63%, 136-8°, stable when kept at 0°.

III: a, C₆H₅, 64%, 99,5-101,0°; the same compound was also obtained from the reaction of N-chloro benzenesulfonylformimidoyl chloride (ref. 1) and cyclohexene episulfide, 74%; b, p-CH₃C₆H₄, 58%, 63,5-65°; c, p-CH₃OC₆H₄, 63%, 101-3°; d, p-ClC₆H₄, 78%, 89-91°; e, p-O₂NC₆H₄, 81%, 129-31°.

IV: a, CH₃, 77%, 109-10°; b, C₆H₅, 84%, 167,5-68°; c, p-O₂NC₆H₄, 72%, 190-2°. All compounds had elemental analyses and spectroscopic properties in agreement with the proposed structures. All compounds having a C=N double bond showed strong adsorption at or near 1580 cm⁻¹ in the infrared spectrum.

References:

- (1) M.S.A. Vrijland and J.Th. Hackmann, *Tetrahedron Letters* **1970**, 3763.
- (2) H. Kristinsson, *Tetrahedron Letters* **1973**, 4489.