ADDITION OF CHLORINE TO THE CYANOGEN BOND IN SULFONYL CYANIDES

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Chlorine adds to activated cyano groups to give substituted N-chloro-formimidoyl chlorides, as was reported by several authors.^{2,3,4.}

The enhanced reactivity of the cyano group in sulfonyl cyanides with nucleophilic reagents and in cycloaddition reactions was pointed out by van Leusen and Jagt.^{5,6}.

We now wish to report the readily occuring addition of chlorine to the cyanogen bond in sulfonyl cyanides to give substituted N-chloro sulfonyl formimidoyl chlorides:

The reaction may be performed in a suitable solvent (e.g. CH_2Cl_2 , $CHCl_3$, CCl_4) without a catalyst, at room temperature or above. Quantitative yields however were obtained when the sulfonyl cyanide was heated in a sealed tube with excess chlorine.

So when methane sulfonyl cyanide⁷ was heated with an excess chlorine for 15 h at 100-110[°], N-chloro methylsulfonyl formimidoyl chloride (I, $R=CH_3$) was formed in quantitative yield.

(I) may be purified by distillation (b.p. $70-70.5^{\circ}/0.5 \text{ mm}$; m.p. $46-48^{\circ}$). Correct elemental analysis was obtained. NMR (CCl₄), (singlet at $\tau = 6.73$) IR (C=N absorption at 1580 cm⁻¹) and mass spectral data (m/e 175 (M⁺), 140 (CH₃SO₂CClN⁺), 96 (ClCNCl⁺), 79 (CH₃SO₂⁺), 61 (ClCN⁺) agree with the proposed structure.

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REFERENCES

- This paper is considered to be part II of a series on the Addition of Chlorine to the Cyanogen Bond.
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