

## ADDITION OF CHLORINE TO THE CYANOGEN BOND IN SULFONYL CYANIDES<sup>1</sup>

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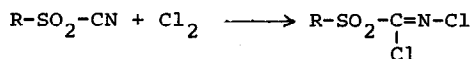
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(Received in UK 11 August 1970; accepted for publication 13 August 1970)

Chlorine adds to activated cyano groups to give substituted N-chloroformimidoyl chlorides, as was reported by several authors.<sup>2,3,4.</sup>

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.<sup>5,6.</sup>

We now wish to report the readily occurring 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.  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ) 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 cyanide<sup>7</sup> was heated with an excess chlorine for 15 h at  $100\text{-}110^\circ$ , N-chloro methylsulfonyl formimidoyl chloride (I,  $\text{R}=\text{CH}_3$ ) was formed in quantitative yield.

(I) may be purified by distillation (b.p.  $70\text{-}70.5^\circ/0.5$  mm; m.p.  $46\text{-}48^\circ$ ). Correct elemental analysis was obtained. NMR ( $\text{CCl}_4$ ), (singlet at  $\tau = 6.73$ ) IR (C=N absorption at  $1580\text{ cm}^{-1}$ ) and mass spectral data ( $m/e$  175 ( $\text{M}^+$ ), 140 ( $\text{CH}_3\text{SO}_2\text{CClN}^+$ ), 96 ( $\text{ClCNCl}^+$ ), 79 ( $\text{CH}_3\text{SO}_2^+$ ), 61 ( $\text{ClCN}^+$ ) agree with the proposed structure.

Other examples are: II, R = C<sub>6</sub>H<sub>5</sub>, m.p. 46-48°, b.p. 124-125°/0.5 mm;  
III, R = p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, m.p. 67-69°; IV, R = p-ClC<sub>6</sub>H<sub>4</sub>, m.p. 83-84°.

## REFERENCES

1. This paper is considered to be part II of a series on the Addition of Chlorine to the Cyanogen Bond.  
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The sulfonyl cyanides used were obtained by a method very similar to that described by Cox and Ghosh, developed independently in our laboratory.