Chlorine adds to activated cyano groups to give substituted N-chloroformimidoyl chlorides, as was reported by several authors.\textsuperscript{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.\textsuperscript{5,6}

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:

\[ R\text{-SO}_2\text{-CN} + \text{Cl}_2 \rightarrow R\text{-SO}_2\text{-C=N-Cl} \]

The reaction may be performed in a suitable solvent (e.g. CH\textsubscript{2}Cl\textsubscript{2}, CHCl\textsubscript{3}, CCl\textsubscript{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\textsuperscript{7} was heated with an excess chlorine for 15 h at 100-110\textdegree{C}, N-chloro methylsulfonyl formimidoyl chloride (I, R=CH\textsubscript{3}) was formed in quantitative yield.

(I) may be purified by distillation (b.p. 70-70.5\degree{C}/0.5 mm; m.p. 46-48\degree{C}). Correct elemental analysis was obtained. NMR (CCl\textsubscript{4}), (singlet at \( \tau = 6.73 \)) IR (C=N absorption at 1580 cm\textsuperscript{-1}) and mass spectral data (m/e 175 (M\textsuperscript{+}), 140 (CH\textsubscript{3}SO\textsubscript{2}CCl\textsuperscript{+}), 96 (ClCNCI\textsuperscript{+}), 79 (CH\textsubscript{3}SO\textsubscript{2}\textsuperscript{+}), 61 (ClCN\textsuperscript{+}) agree with the proposed structure.
Other examples are: II, $R = C_6H_5$, m.p. 46-48°, b.p. 124-125°/0.5 mm;
III, $R = p-CH_3C_6H_4$, m.p. 67-69°; IV, $R = p-ClC_6H_4$, 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.
   Part I is: J. Geevers, J.Th. Hackmann and W.P. Trompen,

The sulfonyl cyanides used were obtained by a method very similar to that described by Cox and Ghosh, developed independently in our laboratory.