Oxidation of Thiocyanates to Sulphonyl Cyanides

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Summary Reaction of aliphatic and aromatic thiocyanates with *m*-chloroperbenzoic acid gives the corresponding sulphonyl cyanides.

THE first synthesis of a sulphonyl cyanide, $R{\cdot}SO_2{\cdot}CN$, was recently reported by Van Leusen and his co-workers[1] who prepared this new functional group by the reaction of nitrosyl chloride with tolyl-*p*-sulphonylmethlenetriphenylphosphorane in the presence of pyridine. Contrary to the statement of Van Leusen that sulphonyl cyanides cannot be prepared by the oxidation of thiocyanates, we describe a new synthesis of sulphonyl cyanides by that route. When allowed to react in hexane at 60° for 20 hr., *p*-tolyl thiocyanate and *m*-chloroperbenzoic acid (MCPBA) gave, after work-up,† toluene-*p*-sulphonyl cyanide in 79% yield. The physical and spectral properties were identical to those reported by Van Leusen.

Similar treatment of ethyl thiocyanate with MCPBA in hexane at 25° for 24 hr. gave, in 6% yield, ethanesulphonyl cyanide, b.p. 65—67°/3 mm. In addition to the elemental analysis, proof of structure follows from the CN and SO_2 stretching bands in the i.r. spectrum at 2197, and 1380 and 1170 cm.$^{-1}$, respectively. The mass spectrum had *m/e* 93 ($CH_3{\cdot}CH_2SO_2^+$), 69 ($^+SO_2$), 48 (SO^+) and 29 ($CH_3{\cdot}CH_2^+$). The n.m.r. spectrum ($CDCl_3$) consisted of a triplet at δ 1·40, J 7·3 c./sec. (3H) and a quartet at δ 3·4, J 7·3 c./sec. (2H). In addition to the desired product, *m*-chlorobenzoic acid and *m*-chlorobenzoyl peroxide were the only products isolated from the oxidation of the aliphatic thiocyanate. The presence of the peroxide and the failure to isolate other materials implies that the low yield may, in part, be due to a free-radical decomposition of the starting material, intermediate, or product into unknown volatile products.

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† The reaction mixture was filtered, to remove *m*-chlorobenzoic acid. The hexane was evaporated and the residue dissolved in benzene and chromatographed over silica gel prior to recrystallization.

[1] A. M. Van Leusen, A. J. Iedema, and J. Strating, *Chem. Comm.*, 1968, 440.