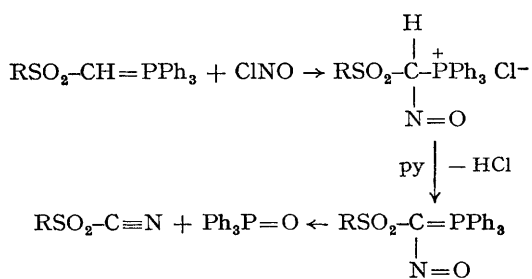


Sulphonyl Cyanide, a New Functional Group

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WE report the synthesis of a new functional group in which a cyano-function is attached directly to the sulphur atom of a SO_2 group. Such sulphonyl



(R = *p*-tolyl)

cyanides cannot be prepared by reaction of sulphonyl halides with potassium,¹ copper(I),² silver² or lithium² cyanides, by oxidation of thiocyanates,^{2,3}

or by addition of hydrogen cyanide² to photochemically generated sulphenes.⁴ However, reaction of nitrosyl chloride (1.5 equiv.) with tolyl-*p*-sulphonylmethylenetriphenylphosphorane⁵ in the presence of pyridine⁶ (2 equiv.) in dichloromethane (at -40°) gives toluene-*p*-sulphonyl cyanide in yields of 84–96%, and triphenylphosphine oxide (*ca.* 85%).

Toluene-*p*-sulphonyl cyanide is a fairly stable compound, which could be distilled, m.p. 46–48° (from hexane), b.p. 105–106/1 mm. The n.m.r. spectrum (CCl_4) displays the usual pattern for a toluene-*p*-sulphonyl group, A_2B_2 quartet at τ 2.05 and 2.50, J 9 c./sec. (4 H), singlet at τ 7.45 (3 H), and the i.r. spectrum (molten sample) shows strong bands at 2190 ($\text{C}\equiv\text{N}$), 1375 and 1170 cm^{-1} (SO_2). Both sulphonyl bands are shifted to higher frequencies, as with sulphonyl halides, due to the electron-withdrawing halogen.⁷ The u.v. spectrum (cyclohexane) has a maximum at 238 m μ (ϵ 13,500)

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and shoulders at $270\text{ m}\mu$ (ϵ 180) and $278\text{ m}\mu$ (ϵ 140). The mass spectrum is relatively simple and demonstrates the loss of a CN moiety by peaks at m/e 181 (M^+), 155 ($\text{C}_7\text{H}_7\text{SO}_2^+$) and a metastable one at 132.7 (for $181 \rightarrow 155$).

The spectra, together with the elemental analysis, suggest only one alternative structure, a sulphonyl isocyanide $\text{RSO}_2\text{-N}\equiv\text{C}$, since the i.r. band at 2190 cm^{-1} might apply to both isomers.⁸ However, the isocyanide structure is unlikely, as similar reactions of nitrosyl chloride and acylmethylenephosphoranes lead to the well-known acyl cyanides.⁶ Formation of a sulphonyl isocyanide

would require either a completely different course of reactions, or isomerisation of initially formed sulphonyl cyanide. The latter is unlikely since only isomerisations of isocyanides to cyanides have been reported.⁹

Reaction of toluene-*p*-sulphonyl cyanide with phenylmagnesium bromide yields benzonitrile. A possible explanation of this reaction is the addition of the Grignard reagent to the triple bond of toluene-*p*-sulphonyl cyanide followed by 1,2-elimination of a magnesium toluene-*p*-sulphinat (or sulphinic acid after hydrolysis of the complex).

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¹ G. McGowan, *J. prakt. Chem.*, 1884, **30**, 280.

² A. M. van Leusen, P. H. Brouwer, R. B. Helmholdt, and J. Strating, unpublished observations.

³ H. Böhme and U. Scheel, *Chem. Ber.*, 1967, **100**, 347.

⁴ R. J. Mulder, A. M. van Leusen, and J. Strating, *Tetrahedron Letters*, 1967, 3057.

⁵ A. J. Speziale and K. W. Ratts, *J. Amer. Chem. Soc.*, 1965, **87**, 5603.

⁶ The use of pyridine in similar syntheses of acylcyanides from acylmethylenetriphenylphosphorane allows a one-step reaction and conversion of all phosphorane into acylcyanide (A. M. van Leusen, Miss G. H. J. van Buuren, and J. Strating, unpublished results). K. Akiba, C. Eguchi, and N. Inamoto (*Bull. Chem. Soc. Japan*, 1967, **40**, 2983) report the same reactions either as a two-step process, or as a single-stage reaction in which only half of the acylmethylenephosphorane is converted. Another approach to acylcyanides is the reaction of β -ketophosphonium salts with alkyl-nitrites (E. Zbiral and L. Fenz, *Monatsh.*, 1965, **96**, 1983).

⁷ C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press, New York, 1963, p. 305.

⁸ Ref. 7, p. 268.

⁹ J. Casanova, N. D. Werner, and R. E. Schuster, *J. Org. Chem.*, 1966, **31**, 3473.