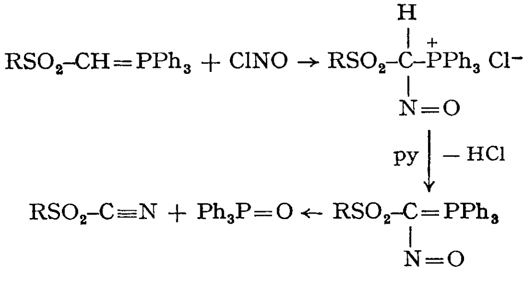
Sulphonyl Cyanide, a New Functional Group

By A. M. VAN LEUSEN*, A. J. W. IEDEMA, and J. STRATING

(*Department of Organic Chemistry, Groningen University, Bloemsingel* 10, *Groningen, The Netherlands*)

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 cyanides cannot be prepared by reaction of sulphonyl halides with potassium,[1] copper(I),[2] silver[2] or lithium[2] cyanides, by oxidation of thiocyanates,[2,3] or by addition of hydrogen cyanide[2] to photolytically generated sulphenes.[4] However, reaction of nitrosyl chloride (1·5 equiv.) with tolyl-*p*-sulphonylmethylenetriphenylphosphorane[5] in the presence of pyridine[6] (2 equiv.) in dichloromethane (at −40°) gives toluene-*p*-sulphonyl cyanide in yields of 84—96%, and triphenylphosphine oxide (*ca.* 85%).



$$RSO_2\text{-}CH{=}PPh_3 + ClNO \rightarrow RSO_2\text{-}\overset{\displaystyle H}{\underset{\displaystyle N{=}O}{C}}\text{-}\overset{+}{P}Ph_3\ Cl^-$$

$$\xrightarrow[-HCl]{py}$$

$$RSO_2\text{-}C{\equiv}N + Ph_3P{=}O \leftarrow RSO_2\text{-}\underset{\displaystyle N{=}O}{C}{=}PPh_3$$

(R = *p*-tolyl)

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 (C≡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 mμ (ϵ 13,500) and shoulders at 270 mμ (ε 180) and 278 mμ (ε 140). The mass spectrum is relatively simple and demonstrates the loss of a CN moiety by peaks at m/e 181 (M^+), 155 ($C_7H_7SO_2^+$) and a metastable one at 132·7 (for 181 → 155).

The spectra, together with the elemental analysis, suggest only one alternative structure, a sulphonyl isocyanide $RSO_2{-}N{\equiv}C$, 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*-sulphinate (or sulphinic acid after hydrolysis of the complex).

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

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[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 alkylnitrites (E. Zbiral and L. Fenz, *Monatsh.*, 1965, **96**, 1983).

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