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A SIMPLE SYNTHESIS OF SULPHONYL CYANIDES

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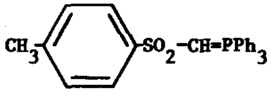
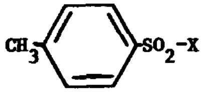
In a recent communication (1), the first synthesis of a compound containing the elusive sulphonyl cyanide moeity was described. Thus, on treatment with nitrosyl chloride and pyridine, the phosphorane (I) gave toluene p-sulphonyl cyanide (II). Although compounds of this type do not arise from a variety of direct approaches (1), it appeared to us probable that they should result from the treatment of sulphinate anions with a cyanogen halide (2).



(I)



(II, X = CN)

(III, X = Br)

Accordingly, when an aqueous solution of sodium toluene p-sulphinate was treated with excess cyanogen chloride at room temperature, the corresponding cyanide (II) was obtained in excellent yield. This material, m.p. 49-50° [lit. (1), 46-48°] analysed correctly for $C_8H_7NO_2S$ and displayed spectral characteristics identical to those reported previously.

The generality of the method was established by saturating, in situ, an aqueous solution of a variety of sodium sulphinates with cyanogen chloride. (See Table)

In the cyanogen halide series, the polarity of the carbon-halogen bond is such that, whilst cyanogen chloride almost always reacts with displacement of the chloride anion, the corresponding bromide sometimes acts as a source of positive bromine (3). It was not surprising to find that on treatment of sodium toluene p-sulphinate with cyanogen bromide, we obtained only the corresponding sulphonyl bromide (III).

Product, RSO_2CN	m.p.	b.p. and n_D	Overall Yield % and Method*
$4\text{-}CH_3.C_6H_4\text{-}$	49-50°		89;A
$C_6H_5\text{-}$	19-20°	73° (0.1 mm.)	92;A
$4\text{-}Cl.C_6H_4\text{-}$	56-58°		97;B
$4\text{-}Br.C_6H_4\text{-}$	96-98°		63;B
$4\text{-}F.C_6H_4\text{-}$		69-70° (0.08 mm.) n_D^{19} 1.5172	42;B
$4\text{-}(CH_3.CONH).C_6H_4\text{-}$	163-164°		93;A
$4\text{-}CH_3O.C_6H_4\text{-}$	67-68°		87;B
$3\text{-}CO_2H,4\text{-}Cl.C_6H_3\text{-}$	137°		22;B
$4\text{-}Cl,3\text{-}NO_2.C_6H_3\text{-}$**	81-82°		35;B
$n\text{-}C_6H_{13}\text{-}$		75-77° (0.2 mm.) n_D^{24} 1.4390	15;C
$CH_3\text{-}$***		n_D^{24} 1.4281	93;B

* The sulphinic acid salts were obtained by a variety of methods: A, commercially available; B, by reduction of the corresponding sulphonyl halide; C, by treatment of an alkyl magnesium halide with sulphur dioxide. The yield is that obtained overall from the sulphinic acid or salt, the sulphonyl halide or the alkyl halide respectively.

** Decomposes during recrystallization from petroleum.

*** Not purified; decomposes over a period of hours at room temperature.

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