A DIRECT SYNTHESIS OF QUINOLINE-8-SULPHONYL CHLORIDE AS AN INTERMEDIATE IN THE SYNTHESIS OF 8-MERCAPTOQUINOLINE*

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The analytical applications of 8-mercaptoquinoline have been investigated in some detail over the past decade and syntheses of this compound have been described by Edinger,[1] Bankovskis,[2] Ponci and Gialdi,[3] Badger and Buttery,[4] Sherchuk and Lukša,[5] and Lee.[6] Each of these syntheses requires three steps for the conversion of quinoline to 8-mercaptoquinoline, the steps being:

(i) preparation of quinoline-8-sulphonic acid
(ii) conversion of this acid to quinoline-8-sulphonyl chloride
(iii) conversion of quinoline-8-sulphonyl chloride to 8-mercaptoquinoline.

It has been found possible to simplify and shorten the overall synthesis by replacing steps (i) and (ii) with a single step involving the treatment of quinoline directly with chlorosulphonic acid. The experimental conditions for this reaction were found to be fairly precise and it was found that a temperature of reaction outside the range $140°\pm5°$ resulted in a lower yield and a more impure product.

The quinoline-8-sulphonyl chloride was found to have a tendency to be unstable and could not be stored for any length of time.

The final reduction to 8-mercaptoquinoline was carried out as described by Sherchuk and Lukša.[5]

Experimental

Quinoline-8-sulphonyl Chloride.—Redistilled quinoline (7 g) was added, drop by drop, over 1 hr, to chlorosulphonic acid (25 ml) contained in a three-necked flask fitted with a thermometer, water condenser (with $CaCl_2$ tube), and dropping funnel. The temperature of the chlorosulphonic acid was $140°\pm5°$ and this temperature was maintained for a further $3\frac{1}{2}$ hr after the last of the quinoline had been added. The reaction mixture was then cooled and the dark brown liquid was poured with caution into crushed ice (150 g). The resulting solution was neutralized with sodium carbonate and extracted with ether. The ether extract was decolourized with charcoal and evaporated on a steam-bath until only 2–3 ml of solvent remained. This small amount of solvent was decanted off and discarded. The white crystalline quinoline-8-sulphonyl chloride which remained was dried *in vacuo* over phosphorus pentoxide for 30 min; yield 3·0 g (24%), m.p. 126–128° (lit.: 118–122°;[6] 124–126°;[7] 128·5–129°[4]) (Found: C, 47·0; H, 2·6; N, 6·0%. Calc. for $C_9H_6ClNO_2S$: C, 47·5; H, 2·7; N, 6·1%).

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