A New Synthetic Route to Iodomethyl Sulfoxides[1]

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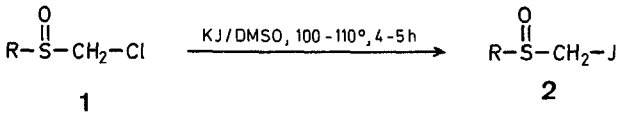
In recent years much interest has been directed to the chemistry of chloromethyl sulfoxides and a number of synthetic methods[2-5] are now available. However, little is known about the corresponding iodo derivatives, which were reported[6] to be accessible by the reaction of sulfinyl chloride with diazomethane in the presence of potassium iodide.

During the study on some problems in this laboratory we have found that iodomethyl sulfoxides can be prepared easily by Finkelstein reaction of chloromethyl sulfoxides (Scheme **A**).

We now wish to communicate the results.



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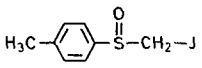
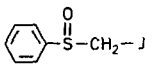
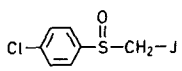
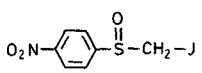
Scheme **A**

The reaction proceeds quite cleanly on heating both reactants at 100–110° for 4–5 h in dimethyl sulfoxide as a solvent, iodomethyl sulfoxides being produced in 80–85% yields. Some representative examples are shown in the Table.

Chloromethyl sulfoxides have become readily available in this laboratory by oxidation of chloromethyl sulfides with

Table. Preparation of Aryl Iodomethyl Sulfoxides **2**

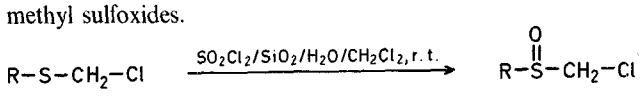
Product		Yield[a] [%]	m.p.	Molecular formula[b]	^{1}H-N.M.R. data[c] for $-CH_2J$ δ ppm	J Hz	(AB q) Δ_{AB}
2a		81 (70)	66°	C_8H_9JOS (280.1)	4.43, 4.19	10.3	14.4
2b		80 (72)	88°	C_7H_7JOS (266.1)	4.42, 4.18	10.2	14.4
2c		84 (67)	106°	C_7H_6ClJOS (300.5)	4.49, 4.18	10.3	15.5
2d		85 (62)	155°	$C_7H_6JNO_3S$ (311.1)	4.50, 4.23	10.8	16.2

[a] Yields (based on chloromethyl sulfoxides) of the crude crystalline products, which were checked by ^{1}H-N.M.R. and proved to be practically pure, are nearly quantitative. Values in brackets are based on methyl sulfides.

[b] All compounds gave satisfactory microanalyses (C ±0.28%, H ±0.28%, J ±0.28%).

[c] Determined in $CDCl_3$ using TMS as an internal standard.

sulfuryl chloride in the presence of a small amount of wet silica gel (Scheme **B**)[2]. Chloromethyl sulfides are known to be synthesized by chlorination of methyl sulfides with sulfuryl chloride (Scheme **C**)[7]. Therefore, combination of Schemes **A**, **B**, and **C** constitutes a new convenient and facile synthetic route starting with methyl sulfides to iodomethyl sulfoxides.



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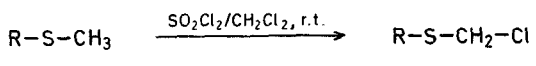
Scheme **B**



4 **3**

Scheme **C**

Synthesis of Iodomethyl Phenyl Sulfoxide (2b); Typical Procedure: To a stirred solution of methyl phenyl sulfide (5 g, 40.3 mmol) in dichloromethane (20 ml) was added sulfuryl chloride (6.53 g, 48.4 mmol) in dichloromethane (20 ml) and heated under reflux for 2 h. The mixture was cooled to room temperature, water (5 g, 278 mmol), silica gel (5 g silicic acid, Mallinckrodt, 100 mesh) and then, with stirring, a solution of sulfuryl chloride (6.53 g, 48.4 mmol) in dichloromethane (20 ml) were added to the reaction mixture. Stirring was continued for 2 h at room temperature and finely powdered anhydrous potassium carbonate (4–5 g) was added. After stirring for another 0.5 h, the mixture was filtered and the filtrate was evaporated in vacuo to give *chloromethyl phenyl sulfoxide*; yield: 6.3 g (90%).

Chloromethyl phenyl sulfoxide (350 mg, 2 mmol) and potassium iodide (664 mg, 4 mmol) were dissolved into commercial dimethyl sulfoxide (2 ml) and heated at 100–110° for 4 h. On dilution with water, iodomethyl phenyl sulfoxide precipitated as yellow needles, recrystallization of which from isopropyl alcohol gave the pure compound; yield: 426 mg (80% yield based on chloromethyl phenyl sulfoxide) m.p. 88° (lit.[6] m.p. 84–86°).

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F. E. Hardy, P. R. H. Speakman, P. Robsen, *J. Chem. Soc.* [C] **1969**, 2334.
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