

Oxygen-18 Tracer Study on the Reduction of Arylsulfonyl Chloride with Zinc

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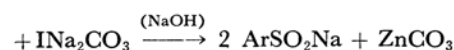
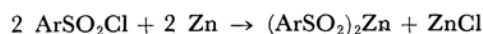
Optically active, ^{18}O -labeled sulfoxides are very convenient for studying the nature of substitution reactions on the trivalent sulfur atom, while ^{18}O -labeled arylsulfinic acids are essential starting materials for the preparation of optically active and ^{18}O -labeled sulfoxides.¹⁾ Meanwhile sulfonyl chlorides are known to be reduced by treating with metallic zinc to the corresponding sulfinic acids.²⁾ In this note, we wish to report a tracer study on this reduction and a convenient procedure for the preparation of the arylsulfinic acid- ^{18}O . ^{18}O -Labeled arylsulfonyl chloride can be prepared readily by treating aryl mercaptan with chlorine in a media containing H_2^{18}O . If there is no oxygen exchange between the reactants and water during the reduction of the ^{18}O -labeled sulfonyl chlorides, this zinc reduction of sulfonyl chlorides will be definitely simpler and better than the conventional procedure in which the ^{18}O -labeled sulfinic acids are usually obtained by the hydrolysis of the corresponding unlabeled sulfinyl chlorides with ^{18}O -enriched water,³⁾ thereby the sulfinic acids obtained contain only a half the concentration of ^{18}O of

that of ^{18}O -enriched water used. An ^{18}O -labeled arylsulfonyl chloride was treated with zinc dust in hot water, and the sodium arylsulfinate was obtained by the successive treatments with sodium hydroxide and sodium carbonate according to the method described by Whitmore and Hamilton.²⁾ Sodium arylsulfinate thus obtained was converted to the corresponding sulfinic acid by neutralization and also to sulfinyl chloride by the treatment with

TABLE 1. RESULTS OF ^{18}O -ANALYSES

| R | (Atom% ^{18}O) | | | |
|---|--------------------------|-------------------------|------------------------|----------------|
| | RSO_2Cl | RSO_2Na | RSO_2H | RSOCl |
| C_6H_5 | 1.14 | 1.14 | 1.15 | 1.13 |
| <i>p</i> - $\text{CH}_3\text{-C}_6\text{H}_4$ | 1.59 | 1.50 | 1.52 | — |
| <i>p</i> - $\text{Br-C}_6\text{H}_4$ | 1.43 | 1.39 | 1.40 | — |

Natural CO_2 ; 0.206 atm% ^{18}O



thionyl chloride, respectively. The results of ^{18}O -analyses of these products are listed in Table 1. As shown in Table 1, the ^{18}O -concentrations of all the products obtained were found to be identical to that of the arylsulfonyl chloride started.

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14) E. S. Leuchenko, N. Ya. Derkach and A. V. Kirsonov, *Zh. Obshch. Khim.*, **31**, 1971 (1962).