

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

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(Received April 12, 1968)

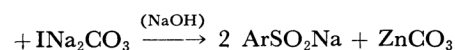
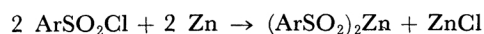
Optically active, ^{18}O -labeled sulfoxides are very convenient for studying the nature of substitution reactions on the trivalent sulfur atom, while ^{18}O -labeled arylsulfinic acids are essential starting materials for the preparation of optically active and ^{18}O -labeled sulfoxides.¹⁾ Meanwhile 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
$p\text{-CH}_3\text{-C}_6\text{H}_4$	1.59	1.50	1.52	—
$p\text{-Br-C}_6\text{H}_4$	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.

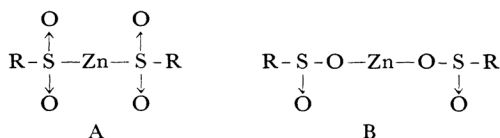
1) K. K. Andersen, *Tetrahedron Letters*, **1962**, 93; H. Phillips, *J. Chem. Soc.*, **1925**, 2575.

2) F. C. Whitmore and F. H. Hamilton, "Organic Syntheses," Coll. Vol. I, p. 492 (1956).

3) M. Kobayashi, M. Terao and A. Yamamoto, *This Bulletin*, **39**, 802 (1966).

This reduction has been known to proceed stoichiometrically according to the following manner.

At first the chlorine atom of the sulfonyl chloride is considered to be replaced by zinc to form a complex (I), the intermediary product, by the same fashion as in the preparation of zinc dialkyls from alkyl halides and metallic zinc.⁴⁾ This complex (I) would be stabilized by the coordination of several water molecules around zinc atom of (I). When the complex (I) is decomposed by the treatment with alkali, sodium arylsulfinate is formed. In fact, Haszeldine and Kidd have successfully isolated zinc trifluoromethanesulfinate, $(\text{CF}_3\text{SO}_2)_2\text{Zn}\cdot 4\text{H}_2\text{O}$, as an intermediate in this zinc reduction.^{5,6)} The complex (I) would assume either one of the following form, A or B, however, in view of the fact that the oxygen atom of the sulfinate ion is more basic than the sulfur atom, the form B seems to be more plausible.⁷⁾



Since there was no oxygen exchange in the next step, *i. e.*, the reaction between the complex (I) and alkali hydroxide, the process involving the ligand exchange with hydroxide ion is the only conceivable path for the formation of sodium aryl sulfinate.

4) E. G. Rochow, D. H. Hurd and R. L. Lewis, "The Chemistry of Organometallic Compounds," John Wiley & Son, New York, N. Y. (1967), p. 100.

5) R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, **1955**, 2901.

6) The structure of the product of dimethylzinc and sulfur dioxide has been also proposed to be $(\text{CH}_3\text{SO}\cdot\text{O})_2\text{Zn}$ based on IR spectra; N. A. D. Carey and H. C. Clark, *Can. J. Chem.*, **46**, 649 (1968).

7) We do not intend to specify the bonding of this complex which would assume either ionic or covalent bonding. Presumably, however, Zn-O bond of I is near covalent. See also the related observation that *p*-tolylsulfinyl copper complex has O-Cu bond with considerable covalent character; D. A. Langs and C. R. Hare, *Chem. Commun.* (London), **1967**, 853.

Experimental

¹⁸O-Labeled Arylsulfonyl Chloride. A mixture of aryl mercaptan (0.1 mol) and ¹⁸O-enriched water (0.22 mol, 1.60 atom% ¹⁸O) was cooled in an ice bath, and chlorine gas was passed till the color of the mixture became pale yellow. Then the mixture was poured into ice water and extracted with chloroform. The extract was washed with 10% aqueous sodium carbonate, 10% aqueous sodium thiosulfate and water successively. The ¹⁸O-labeled arylsulfonyl chloride was distilled or recrystallized from *n*-hexane several times. RSO_2Cl ; [R, mp or bp(°C)(lit.), yield(%), atom% ¹⁸O]. C_6H_5 , 77—78/2 mmHg (147/45 mmHg),⁸⁾ 90, 1.14. *p*-CH₃-C₆H₄, 69(69),⁹⁾ 93, 1.53, 1.59. *p*-Br-C₆H₄, 73—74 (74—75),¹⁰⁾ 91, 1.43.

The Reduction of Arylsulfonyl Chloride with Zinc was carried out following the procedure described by Whitmore and Hamilton,²⁾ using ¹⁸O-labeled arylsulfonyl chloride (0.06 mol). The sodium arylsulfinate dihydrate was obtained in a good yield, 75—90%. The dihydrate was dehydrated *in vacuo* for 5 hr at 120—130°C for the mass analysis.

¹⁸O-Labeled Arylsulfonic Acid was prepared by the careful neutralization of the ¹⁸O-labeled sodium arylsulfinate with hydrochloric acid. It was recrystallized from *n*-hexane - ether. RSO_3H ; [R, mp(°C)(lit.)]. C_6H_5 , 83(83),¹¹⁾ *p*-CH₃-C₆H₄, 85(85),¹²⁾ *p*-Br-C₆H₄, 113 (114).¹¹⁾

¹⁸O-Labeled Benzenesulfinyl Chloride was prepared from anhydrous sodium benzenesulfinate (1.8 g) and thionyl chloride (4.0 g),¹³⁾ bp 81—82°C/2 mmHg (lit¹⁴⁾ 96—98°C/4 mmHg), yield 1.1 g.

The Mass-spectrometric Analysis was carried out in the form of carbon dioxide gas and the atom% ¹⁸O was calculated from the mass peak heights 44 and 46.

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