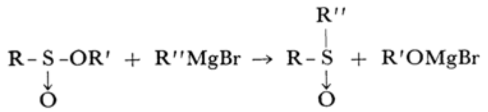
Organic Sulfur Compounds. VII. The Reaction of Methyl *p*-Toluenesulfinate-[sulfinyl-^{18}O] with Phenylmagnesium Bromide

By Michio KOBAYASHI* and Miki TERAO

Department of Chemistry, Yokohama City University, Mutsuura-machi, Kanazawa-ku, Yokohama

(Received November 1, 1965)

The formation of sulfoxides from the sulfinic esters and Grignard reagents has been long known.[1] Recently this method has been utilized for the preparation of the optically active sulfoxides from *l*-menthyl sulfinates and Grignard reagents.[2] Since the configuration of the resulted sulfoxide is opposite to that of the starting sulfinate ester, this reaction has been considered to proceed by a S_N2 type nucleophilic attack on the sulfur atom, with an inversion and displacement of the alkoxide anion[3]:

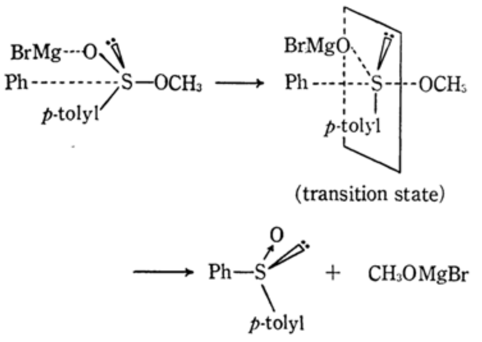


$$\mathrm{R}-\underset{\substack{\downarrow\\ \mathrm{O}}}{\mathrm{S}}-\mathrm{OR'} + \mathrm{R''MgBr} \rightarrow \mathrm{R}-\overset{\substack{\mathrm{R''}\\ |}}{\underset{\substack{\downarrow\\ \mathrm{O}}}{\mathrm{S}}} + \mathrm{R'OMgBr} \qquad (1)$$

However, it has not yet been experimentally established which oxygen atom of the sulfinate ester is replaced. This point should be clarified by an examination of the reaction of a Grignard reagent with sulfinate ester-[sulfinyl-^{18}O].

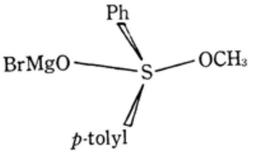
Methyl *p*-toluenesulfinate-[sulfinyl-^{18}O], prepared by the reaction of sodium *p*-toluenesulfinate-^{18}O and ethyl chlorocarbonate in methanol,[4] was therefore treated with phenylmagnesium bromide to give phenyl *p*-tolyl sulfoxide. The excess atom percentage of ^{18}O of this sulfoxide was found to be exactly twice that of the starting methyl sulfinate. This fact can best be explained by postulating the retention of the sulfinyl oxygen atom of the methyl ester in the sulfoxide formed.

The above result is consistent with the currently accepted S_N2 mechanism which may be depicted thus:



(2)

On the other hand, the coordination of the bromomagnesium cation with the sulfinyl oxygen atom of the ester could result in the formation of the sulfonium cation, in which a lone pair electron may enter the 3s orbital and in which three 3p orbitals are available for the formation of three single bonds. The attack of the anionoid phenyl group on the sulfur atom of this cation may occur from the unhindered open side, to give a tetrahedral intermediate (I) using a 3d orbital:



(I)

Similar tetrahedral intermediates with a lone pair in a 3s orbital have been postulated in the reaction of triphenylsulfonium bromide with phenyllithium or *n*-butyllithium.[5]

The elimination of a methoxide anion from I would lead to the sulfoxide with an inverted configuration. Therefore, both the above experimental results and the asymmetric syntheses in the literature can be explained by either the S_N2 mechanism or the tetrahedral intermediate mechanism. The S_N2 mechanism seems to be most plausible in the analogous ester exchange reaction of the sulfinate esters,[6] but in those cases the formation of the sulfonium cation, in which the positive charge on the sulfur atom could cause the $3p^3$ electronic structure discussed above, is impossible.

Experimental

Methyl *p*-Toluenesulfinate-[sulfinyl-^{18}O]. — Prepared from sodium *p*-toluenesulfinate-^{18}O and ethyl

---

* To whom correspondence should be sent: Department of Dhemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya-ku, Tokyo.

[1] H. Gilman, J. Robinson and N. H. Beaber, *J. Am. Chem. Soc.*, **48**, 2715 (1926); H. Gilman and J. Robinson, *Bull. soc. chim. France*, [4] **45**, 636 (1929).

[2] K. K. Anderson, *Tetrahedron Letters*, No. 3, 93 (1962).

[3] K. K. Anderson, *J. Org. Chem.*, **29**, 1953 (1964); K. Mislow, M. M. Green, P. Laur, J. J. Melillo, T. Simmons and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **87**, 1958 (1965).

[4] Part VI of this series: M. Kobayashi and M. Terao, This Bulletin, **39**, 1292 (1966).

[5] V. Franzen and C. Mertz, *Angew. Chem.*, **72**, 416, (1960).

[6] H. Phillips, *J. Chem., Soc.*, **127**, 2552 (1925).

chlorocarbonate in methanol.[4] The ^{18}O atom percentage of this ester was 0.41%.

Phenyl *p*-Tolyl Sulfoxide-^{18}O.—A Grignard reagent prepared from 5.0 g. of bromobenzene and 0.8 g. of magnesium in 20 ml. of ether was added, drop by drop to 2.0 g. of methyl *p*-toluenesulfinate-^{18}O in 30 ml. of benzene. An excess of 3 N hydrochloric acid was then added to the reaction mixture to dissolve the white precipitate, and the organic layer was separated, washed with alkali and water, and dried over magnesium sulfate. The solvent was evaporated, and the oily residue was dissolved in warm petroleum ether and kept overnight. The colorless crystals of sulfoxide which separated were purified by elution chromatography over alumina with benzene to give an analytical sample. The atom percentage of ^{18}O in this product was 0.62%. The calculated ^{18}O atom%, based on the assumption of a reaction of the sulfinyl oxygen of the ester, is 0.61%.

The authors are indebted to Dr. Reiko Kiritani of the Radiation Center of Osaka Prefecture for the analyses of ^{18}O and to Professor Shigeru Oae for the donation of heavy oxygen water.