[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF IOWA STATE COLLEGE]

ARYLSULFONYLMAGNESIUM CHLORIDES AND THEIR REACTIONS WITH DIETHYL SULFATE

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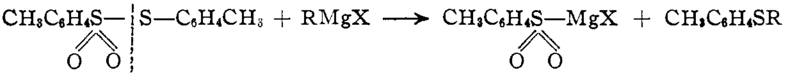
Introduction

Diethyl sulfate has been recommended[1] and used[2] as a reagent for characterizing intermediate compounds formed in reactions involving organometallic compounds. By means of this ester it is possible to replace an -MgX group by the ethyl group and thereby obtain a stable compound that lends itself to ready identification. This replacement reaction occurs with all -CMgX compounds studied, even when the quantity of RMgX compound present is very small.[2b] It is also generally applicable with -NMgX compounds, and with -SMgX compounds where the sulfur is bivalent. Unfortunately it has a very limited application with -OMgX compounds. The same type of replacement reaction is observed with other dialkyl sulfates and with alkyl and halogen alkyl esters of arylsulfonic esters.[3]

The -OMgX compounds, however, are not the only ones that have but a limited application in such replacement reactions. Gilman, Smith and Parker,[4] in connection with the proof of structure of the so-called disulfoxides, have shown that these compounds are true thiosulfonic esters and react as follows with RMgX compounds.



$$CH_3C_6H_4\underset{O\;\;O}{S}-\,\vdots\,S-C_6H_4CH_3 + RMgX \longrightarrow CH_3C_6H_4\underset{O\;\;O}{S}-MgX + CH_3C_6H_4SR \quad (I)$$

In that study the reaction product was heated with diethyl sulfate, prior to hydrolysis, in order to further establish the constitution of the thiosulfonic ester and its mode of reaction with RMgX compounds. However, the diethyl sulfate was apparently without reaction, for no ethyl *p*-tolyl sulfone was obtained from the *p*-tolylsulfonylmagnesium halide. Inasmuch as there exists no reasonable doubt concerning the correctness of Reaction I, it must follow that diethyl sulfate is unsuitable for replacing the -MgX group attached to hexavalent sulfur. Admittedly there is the possibility that the *p*-tolylsulfonylmagnesium halide underwent the following rearrangement.

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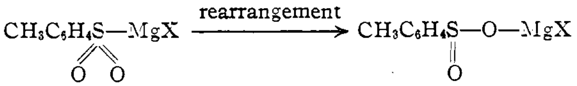
[1] Gilman and Hoyle, THIS JOURNAL, **44**, 2621, 2969 (1922).

[2] (a) Gilman and Kinney, *ibid.*, **46**, 493 (1924); (b) Gilman and Kirby, *ibid.*, **48**, 1733 (1926).

[3] Gilman, Robinson and Beaber, *ibid.*, **48**, 2715 (1926). References to earlier work are given in this paper.

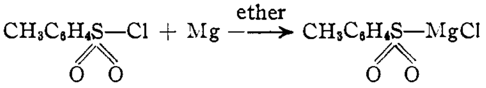
[4] Gilman, Smith and Parker, *ibid.*, **47**, 851 (1925). See, also, the extensive work of Smiles and co-workers, particularly the paper by Miller and Smiles, *J. Chem. Soc.*, **127**, 224 (1925).



$$\mathrm{CH_3C_6H_4\underset{O\ \ O}{\underset{\diagup\diagdown}{S}}—MgX} \xrightarrow{\text{rearrangement}} \mathrm{CH_3C_6H_4\underset{O}{\underset{\|}{S}}—O—MgX} \qquad \text{(II)}$$

There is no ready and exact method for differentiating between the two isomers in Reaction II. For one thing, hydrolysis throws no light on the solution of this problem inasmuch as the product formed is *p*-toluenesulfinic acid, a compound that has been interpreted by some as containing hexavalent sulfur ($\mathrm{CH_3C_6H_4\underset{O\ \ O}{\underset{\diagup\diagdown}{S}}—H}$) and by others as having tetravalent sulfur ($\mathrm{CH_3C_6H_4\overset{O}{\overset{\|}{S}}—OH}$). A third group maintains that we are dealing here with an equilibrium mixture of the two.

Whatever may be the structure, it is obvious that partial or complete rearrangement will give an -OMgX compound, and only a very limited number of such compounds[2a] undergo replacement reactions with diethyl sulfate. In order to have more facts for a possible solution of this problem, a study has been made of the direct reaction between arylsulfonyl chlorides and magnesium in ether. There is no question concerning the structure of compounds like benzenesulfochloride and *p*-toluenesulfochloride. If reaction occurs with magnesium, it should very probably take place as follows.



$$\mathrm{CH_3C_6H_4\underset{O\ \ O}{\underset{\diagup\diagdown}{S}}—Cl} + \mathrm{Mg} \xrightarrow{\text{ether}} \mathrm{CH_3C_6H_4\underset{O\ \ O}{\underset{\diagup\diagdown}{S}}—MgCl} \qquad \text{(III)}$$

The recent work of Tistchenko[5] is related to this study. He showed that carboxylic acid bromides react with magnesium to give acylmagnesium bromides (RC(=O)MgBr).

Reaction has been found to occur between arylsulfonylchlorides and magnesium in ether. Hydrolysis of these new organomagnesium halides gives the corresponding sulfinic acids. Analysis shows them to be arylsulfonylmagnesium chloride-etherates. However, they do not give the corresponding ethyl sulfones when treated with diethyl sulfate. From this, and earlier work,[2a] it may be concluded that the -MgX group attached to sulfur as in a sulfonyl group is not replaceable by an ethyl group when diethyl sulfate is used. Over and against such a conclusion is the possibility that we may be dealing here with an -OMgX compound formed by a rearrangement like that illustrated in Reaction II. The possibility of such a rearrangement is reduced when one considers the conditions of the experiments and unpublished data that have shown diethyl sulfate to be reliable with even those RMgX compounds that are known at times to undergo rearrangement.[6]

[5] Tistchenko, *Bull. soc. chim.*, 37, 623 (1925).

[6] Mr. J. E. Kirby has shown that diethyl sulfate gives normal products with benzylmagnesium chloride, diphenylmethylmagnesium chloride and α-naphthylmethylmagnesium chloride.

Experimental Part

Benzenesulfochloride and Magnesium.—A solution of 35.3 g. (0.2 mole) of benzenesulfochloride in 100 cc. of dry ether was added slowly to 4.9 g. (0.2 mole) of magnesium turnings contained in a 500cc. three-necked flask fitted with a reflux condenser, stirrer and dropping funnel. The reaction was started by means of a crystal of iodine and by warming the reaction flask slightly. A slow reaction took place and the rest of the benzenesulfochloride solution was added over a period of one hour, during which a yellow precipitate formed. After refluxing for one-half hour and stirring at room temperature for twelve hours, the reaction mixture was hydrolyzed with water and 10% hydrochloric acid and then the ether and water layers were separated. The ether layer was extracted with 5% sodium hydroxide and then dried over anhydrous sodium sulfate and distilled at atmospheric pressure to remove the ether. The residue from this distillation was then vacuum distilled and gave 18.8 g. (53.2%) of unused benzenesulfochloride, b. p. 106–108° at 9 mm. (identified by the amide which melted at 152°). The sodium hydroxide extract was acidified and extracted with ether; this extract was dried over anhydrous sodium sulfate and then the ether was evaporated rapidly, leaving 3.5 g. (12.3%) of benzenesulfinic acid, m. p. 83°.

Benzenesulfochloride and Magnesium and Ethyl Sulfate.—In this experiment 35.3 g. (0.2 mole) of benzenesulfochloride in 150 cc. of dry ether was treated with 4.9 g. (0.2 mole) of magnesium under the conditions described in the preceding experiment except that the reaction was started with about 2 g. of activated[7] magnesium. The reaction mixture was refluxed for thirteen hours, then most of the ether was distilled off and 200 cc. of dry toluene added. Thirty and eight-tenths g. (0.2 mole) of diethyl sulfate was then added and the mixture refluxed for eight hours. After standing at room temperature for eighteen hours the reaction mixture was hydrolyzed with 10% hydrochloric acid. The ether layer was extracted with 5% sodium hydroxide and then steam distilled. The residue, not volatile with steam, was a yellow, oily liquid which did not crystallize on cooling to −12° or by slow evaporation of its ether solution. From the distillate were obtained by ether extraction and vacuum distillation 3.1 g. of a liquid boiling from 90 to 105° at 11 mm., probably a mixture of toluene and benzenesulfochloride, and 1.5 g. (4.3%) of unused benzenesulfochloride, boiling from 105 to 120° at 11 mm. (identified by a mixed melting point determination with a known sample of benzenesulfonamide). The sodium hydroxide extract yielded 0.7 g. (2.5%) of benzenesulfinic acid, m. p. 81°. No ethylphenylsulfone was obtained.

***p*-Toluenesulfochloride and Magnesium.**—In an experiment using 57.8 g. (0.3 mole) of *p*-toluenesulfochloride in 250 cc. of dry ether and 7.3 g. (0.3 mole) of magnesium, carried out under the same conditions as the first benzenesulfochloride experiment, 55.1 g. (95.0%) of the *p*-toluenesulfochloride was recovered, but no *p*-toluenesulfinic acid was obtained. In another experiment, 38.1 g. (0.2 mole) of *p*-toluenesulfochloride and 4.9 g. (0.2 mole) of magnesium were used. The reaction was started with about 2 g. of *activated*[7] magnesium and after all of the *p*-toluenesulfochloride was added the reaction mixture was refluxed for ten hours and then stirred at room temperature for ten hours

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[7] This activated magnesium was prepared according to the directions of Gilman, Peterson and Schulze from a powdered magnesium-copper alloy containing 12.75% of copper. A preliminary account of this superior activated magnesium was given at the Philadelphia Meeting of the American Chemical Society in September, 1926. Subsequent mention of it has been made in papers by Hurd and Webb, THIS JOURNAL, **49**, 546 (1927), and Gilman and Harris, *ibid.*, **49**, 1825 (1927). Details of this catalyst are given in a paper by Gilman, Peterson and Schulze to be published early in 1928 in *Rec. trav. chim.*

more. The products obtained after hydrolysis and the general procedures outlined above were 3.0 g. (5.2%) of unused *p*-toluenesulfochloride and 21.7 g. (69.5%) of *p*-toluenesulfinic acid, m. p. 88°. The identity of *p*-toluenesulfinic acid was confirmed by a mixed melting point determination made with an authentic specimen.

***p*-Toluenesulfochloride and Magnesium and Ethyl Sulfate.**—Thirty-eight and one-tenth g. (0.2 mole) of *p*-toluenesulfochloride was added to 4.9 g. (0.2 mole) of magnesium turnings in the same manner as the preceding experiment, using activated magnesium to start the reaction. After the reaction mixture had been refluxed and stirred for nine hours and then stirred at room temperature for eleven hours, about half of the yellow precipitate which had formed was filtered out of the reaction mixture and washed thoroughly with dry ether. Most of the ether was distilled from the remaining reaction mixture and then 200 cc. of dry toluene was added. Twenty-three and one-tenth g. (0.15 mole) of ethyl sulfate was then added and the mixture refluxed for eight hours. From the sodium hydroxide extraction after hydrolysis there was obtained 3.0 g. of *p*-toluenesulfinic acid, m. p. 85° (mixed melting point with an authentic specimen of *p*-toluenesulfinic acid was 87°). The residue, not volatile with steam, was dissolved in ether and allowed to concentrate slowly. At first a few crystals (m. p. 200°) formed and these were removed. Then, in about two weeks, 1 g. of *p*-tolyl-*p*-toluenethiosulfonate, m. p. 77°, was obtained (this was identified by a mixed melting point determination with a known sample of the thiosulfonic ester). The only product recovered from the steam distillate was a small amount of unused *p*-toluenesulfochloride. No ethyl-*p*-tolylsulfone was obtained.

The yellow precipitate which was filtered out of the reaction mixture prior to treatment of the other half with diethyl sulfate, was carefully dried in a desiccator over calcium chloride and analyzed.

Anal. Calcd. for $CH_3C_6H_4SO_2MgCl.(C_2H_5)_2O$: Cl, 12.27. Found: 12.24, 12.22.

Ether (by loss in weight on heating at 110°). Calcd.: 25.7%. Found: 26.1%.

The compound gave a qualitative test for magnesium. When hydrolyzed by dilute hydrochloric acid it gave *p*-toluenesulfinic acid, which was identified by a mixed melting point determination with an authentic specimen.

The arylsulfonylmagnesium chlorides do not give the Gilman and Schulze[8] color test for RMgX compounds. This is as one would expect, inasmuch as a positive color test is not shown by compounds having the -MgX group attached to sulfur or to oxygen.

Summary

Arylsulfonylmagnesium chloride etherates are formed when benzenesulfochloride and *p*-toluenesulfochloride are treated with magnesium in ether. Diethyl sulfate did not replace the -MgCl group in these compounds by an ethyl group.

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[8] Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).