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

# THE REACTION BETWEEN ORGANOMAGNESIUM HALIDES AND THE ESTERS OF SOME SULFUR ACIDS

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## Introduction

The alkyl esters of sulfonic acids react with organomagnesium halides in a manner quite unlike that of all other esters of oxygen or sulfur acids. The typical alkylating action may be represented as follows.

$$2RSO_2O-\text{Alkyl} + 2R'MgX \longrightarrow 2R'-\text{Alkyl} + (RSO_2O)_2Mg + MgX_2 \quad (1)$$

This ready alkylating action of sulfonic esters is also observed towards other classes of compounds such as amines, alcoholates, phenates, etc.[1] The aryl esters of sulfonic acid undergo a different type of reaction, and sulfones and phenols are formed with RMgX compounds.[2]

$$RSO_2-\text{OAryl} + R'MgX \longrightarrow RSO_2R' + MgX-\text{OAryl} \quad (2)$$

However, not even all alkyl sulfonates show an alkylating action towards organomagnesium halides.[3] Ferns and Lapworth[1,4] showed that methyl benzenesulfonate and bornyl *p*-toluenesulfonate gave as chief products the corresponding unsaturated hydrocarbons, menthene and camphene. They also showed that ethyl ethanesulfonate underwent a limited alkylating action (1) towards phenylmagnesium bromide as well as Reaction II leading to sulfones that Strecker[5] reported earlier. Kenyon, Phillips and Turley[6] found that the *p*-toluenesulfonic ester of optically active ethyl lactate when treated with phenylmagnesium bromide, for example, gave ethyl α-bromopropionate and not ethyl α-phenylpropionate. Tistchenko[7] obtained acetaldehyde when acetylmagnesium bromide, $CH_3COMgBr$, was treated with dimethyl sulfate and then hydrolyzed. Fischer and Taube[8] prepared isohydrobenzoin from the reaction between

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[1] Ferns and Lapworth, *J. Chem. Soc.*, **101**, 273 (1912).

[2] Gilman, Beaber and Meyers, THIS JOURNAL, **47**, 2047 (1925).

[3] A paper by Gilman and Beaber [*ibid.*, **47**, 518 (1925)] contains literature references to earlier work on the alkylating action of sulfonic esters towards RMgX compounds. Subsequent to these references is work by Bert [*Bull. soc. chim.*, **37**, 1252 (1925)] and Gilman and Kirby [THIS JOURNAL, **48**, 1733 (1926)]. Ferrario and Fagetti [*Gazz. chim. ital.*, [2] **38**, 630 (1908)] have reported the preparation of tetramethylmethane from *tert.*-butylmagnesium iodide and dimethyl sulfate.

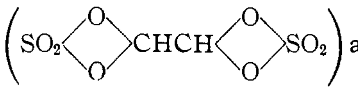
[4] Ferns and Lapworth, *Proc. Chem. Soc. London*, **28**, 18 (1912).

[5] Strecker, *Ber.*, **43**, 1131 (1910).

[6] Kenyon, Phillips and Turley, *J. Chem. Soc.*, **127**, 399 (1925). In connection with the work on sulfinic esters reference should be made to an excellent paper by Phillips [*ibid.*, **127**, 2552 (1925)] on the structure of alkyl sulfinates.

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

[8] Fischer and Taube, *Ber.*, **59**, 851 (1926).

glyoxal sulfate  and phenylmagnesium bromide. This reaction might very correctly be interpreted as a normal alkylating action followed by hydrolysis of the —$OSO_2OMgBr$ group.

Other esters of sulfur acids have been studied. Gilman, Smith and Parker[9] showed that ethyl *p*-toluenethiosulfonate, $CH_3C_6H_4SO_2SC_2H_5$, which is the sulfur analog of ethyl *p*-toluenesulfonate, had no alkylating action and underwent instead a reaction according to Scheme 2 giving phenylethyl sulfide when treated with phenylmagnesium bromide. Bert[10] has recommended the use of di-*n*-butyl sulfite $(C_4H_9O)_2SO$, as a reagent for the preparation of sulfoxides from RMgX compounds. Experiments with di-*n*-butyl sulfite have shown that this sulfinic ester is unlike corresponding sulfonic esters because it shows no alkylating action. Hepworth and Clapham[10a] have studied the reaction between several thiocarboxylic esters and organomagnesium halides.

The present paper reports studies with a wide variety of sulfur esters. It is very interesting to note that none of these sulfur esters behaves like alkyl sulfonates; instead, all appear to react after Scheme 2 which is the general mode of reaction of carboxylic and other esters.[11] The reaction between RMgX compounds and esters of the following acids is reported here: sulfinic, RS(=O)OH; sulfenic, RSOH; thiocarboxylic, RC(=O)SH; thioncarboxylic, RC(=S)OH; and dithiocarboxylic, RC(=S)SH.

## Experimental Part

**Di-*n*-butyl Sulfite.**—Thirty-eight and five-tenths g. or 0.2 mole of di-*n*-butyl sulfite was added slowly to two equivalents of phenylmagnesium bromide. A smooth reaction occurred, and after hydrolyzing and working up in a customary manner there was obtained 16 g. or 40% of diphenyl sulfoxide and 13 g. or 44% of *n*-butyl alcohol. Bert[10] has recommended this general reaction as a preparation for sulfoxides. A careful

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[9] Gilman, Smith and Parker, THIS JOURNAL, **47**, 851 (1925). See also Miller and Smiles, *J. Chem. Soc.*, **127**, 224 (1925).

[10] Bert, *Compt. rend.*, **178**, 1826 (1924). Strecker (Ref. 5) reported earlier the reaction between diethyl sulfite and the Grignard reagent.

[10a] Hepworth and Clapham, *J. Chem. Soc.*, **119**, 1188 (1921).

[11] An article by Gilman and Vernon [THIS JOURNAL, **48**, 1063 (1926)] gives references to studies on other esters. These studies are being extended to all important types of esters. It is highly significant that allyl benzoate when treated with phenyl magnesium bromide appears to give a small quantity of allylbenzene. Peroxides, which might be considered as esters of hydrogen peroxide, show no alkylating action [Gilman and Adams, *ibid.*, **47**, 2816 (1925)]. Likewise, disulfides, which may be considered as esters of hydrogen disulfide, undergo a splitting reaction according to Scheme 2 [Wuyts, *Bull. soc. chim.*, **35**, 166 (1906)]. Furthermore, unpublished work on active halogen compounds shows that the alkyl esters of hypochlorous acid have no alkylating action. Durand and Naves [*ibid.*, **37**, 717 (1925)] have reported recently the reaction between ethyl hypochlorite and the Grignard reagent.

search failed to reveal any *n*-butylbenzene that may have been formed by an alkylating action.

**Ethyl *p*-Toluenesulfinate.**[12]—Fifty g. or 0.27 mole of ethyl *p*-toluenesulfinate was brought into reaction with slightly more than one equivalent of benzylmagnesium chloride. The yield of benzyl-*p*-tolyl sulfoxide was 35.5 g. or 57.2%.

***n*-Butyl *p*-Toluenesulfinate.**—From 20 g. or 0.1 mole of *n*-butyl *p*-toluenesulfinate and an equivalent quantity of phenylmagnesium bromide there was obtained 10 g. or 46% of phenyl-*p*-tolyl sulfoxide and 5.1 g. or 67% of *n*-butyl alcohol. The sulfoxide was identified in two ways: first, some of it was oxidized by hydrogen peroxide in glacial acetic acid[13] to the corresponding sulfone; second, some phenyl-*p*-tolyl sulfide in glacial acetic acid, when allowed to stand for 40 minutes at room temperature with an excess of 30% hydrogen peroxide and then poured into water, gave the phenyl-*p*-tolyl sulfoxide which melts[14] at 124°. Wherever possible in this work the identity of all solids was confirmed by mixed-melting-point determinations.

**Diphenyl Sulfite.**—Two reactions were carried out between 25 g. or 0.107 mole of diphenyl sulfite and 0.3 mole of phenylmagnesium bromide. The yields of diphenyl sulfoxide were 67 and 74%; the yields of phenol were 85 and 87.5%, respectively.

From 21 g. or 0.09 mole of diphenyl sulfite and 0.3 mole of benzylmagnesium chloride, there was obtained 12 g. or 52.2% of dibenzyl sulfoxide and 9 g. or 53% of phenol.

**Methylphenyl sulfenate.**—From 14 g. or 0.1 mole of methylphenyl sulfenate and an equivalent of phenylmagnesium bromide there was obtained 9 g. or 48.4% of diphenyl sulfide. The identity of this sulfide was confirmed by a mixed-melting-point determination of the diphenyl sulfone prepared from it by oxidation in glacial acetic acid solution with 30% hydrogen peroxide.[13]

In an effort to increase the yield of sulfide, the slightly charred residue in the distilling flask was heated further; 1 g. or 5% of diphenyl sulfoxide distilled. The formation of diphenyl sulfoxide is very interesting because it indicates that a splitting according to Scheme 1 as well as 2 had taken place. However, no toluene was noted, and this should have formed if there was an alkylating action (1). The diphenyl sulfoxide very probably was not formed by the oxidation of diphenyl sulfide during distillation, inasmuch as a comparable distillation of pure diphenyl sulfide showed no diphenyl sulfoxide. It is possible that a very limited alkylating action occurs here, and that because of the small-sized run a very small quantity of toluene was not detected. A much larger run is to be made.

**Ethyl Thiolbenzoate.**—The reaction between 12 g. or 0.075 mole of ethyl thiolbenzoate and three equivalents of phenylmagnesium bromide gave 15 g. or 78% of triphenylcarbinol and ethyl mercaptan. A special search failed to reveal any ethylbenzene.

**Ethyl thionbenzoate.**[15]—One-tenth mole of ethyl thionbenzoate was added to four

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[12] This experiment was carried out by L. E. Smith.

[13] Gilman and Beaber, THIS JOURNAL, **47**, 1449 (1925). See p. 1451 of this reference for a consideration of the merits of the hydrogen peroxide-oxidation method for the characterization of sulfides and sulfoxides. Knoll [*J. prakt. Chem.*, **113**, 40 (1926)] has just described a good method for the preparation of sulfoxides from sulfides.

[14] Temperatures recorded in this paper are uncorrected.

[15] Ethyl thionbenzoate was prepared according to the general method of Matsui, *Mem. Coll. Sci. Eng. Kyoto*, **1**, 285 (1908); *C. A.*, **3**, 2697 (1909). It distilled at 112–120° (11 mm.).

It is interesting to note in this connection that Delépine [*Compt. rend.*, **153**, 279 (1911)] prepared thion esters from methyl chlorothiocarbonate, $ClCSOCH_3$ and RMgX compounds. Although these esters were prepared by adding the methyl chlorothioequivalents of phenylmagnesium bromide. After hydrolysis a white solid separated that is very soluble in alcohol, chloroform and benzene, but insoluble in ether. This compound contains magnesium, but does not undergo ready hydrolysis in 10% hydrochloric acid. However, when allowed to stand for four days with the dil. hydrochloric acid solution, an oil separated and this was identified as benzophenone.

The ether layer gave no ethyl benzene on distillation, but from the oil remaining after the ether had been distilled there was obtained 0.5 g. of large crystals of a compound that melted at 143° and contained sulfur. Distillation of the oil gave more benzophenone and 2 g. of a compound or a mixture of compounds containing sulfur that boiled between 184–210° (15 mm.) and melted between 110–115°. The yield of benzophenone was 5.6 g. or 28.1%.

**Ethyl Dithiobenzoate.**—Bromomagnesium dithiobenzoate, $C_6H_5CSSMgBr$, was prepared from phenylmagnesium bromide and carbon disulfide according to the method of Houben.[16] To this mixture in ether there was added one equivalent of diethyl sulfate. After being refluxed for an hour, the ether solution yielded on distillation 9% of ethyl dithiobenzoate boiling between 155° and 160° (15 mm.).[17]

Seventeen and five-tenths g. or 0.09 mole of ethyl dithiobenzoate was added to 0.35 mole of phenylmagnesium bromide. After the mixture had been refluxed for two hours, 35 g. or 0.26 mole of benzoyl chloride was added in order to determine the mode of addition of phenylmagnesium bromide by replacing the —MgBr by the benzoyl group. After hydrolysis with iced hydrochloric acid, a compound separated at the ether-acid interface. This melted at 181–183° when dissolved in benzene and precipitated by petroleum ether. It very probably is triphenylmethyl thiobenzoate $(C_6H_5)_3CSCOC_6H_5$, which melts at 184–185°. This proves that the phenyl group of phenylmagnesium bromide adds to the carbon of the thiocarbonyl group (=C=S) and the —MgBr to sulfur, as is to be expected.

In addition to the small amount of this ester, there was obtained 1.5 g. of thiobenzoyl disulfide $(C_6H_5CSS—)_2$; m. p., 115–116°. This disulfide was probably formed by the oxidation of dithiobenzoic acid, formed by hydrolysis of some unaltered bromomagnesium dithiobenzoate, $C_6H_5CSSMgBr$.

## Summary

No alkylating action has been observed in the reactions between organomagnesium halides and esters of sulfinic, sulfenic, thiocarboxylic, thioncarboxylic and dithiocarboxylic acids.

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carbonate to cold ether solutions of the Grignard reagents, no by-products were obtained by Delépine to indicate that a reaction had taken place under these conditions between the thion ester and the RMgX compound present in excess in the early part of the reaction.

[16] Houben, *Ber.*, **39,** 3219 (1906); **43,** 2481 (1910); **44,** 3226 (1911).

[17] The boiling point of the ester as prepared by another method by Bloch [Ger. pat. 214,888, *Chem. Zentr.*, **80,** 1780 (1909)] is 165–168° (19 mm.).