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

THE CONSTITUTION OF DISULFOXIDES[1]

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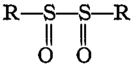
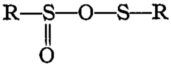
Introduction

The so-called disulfoxides have been known for about 60 years, and although much work has been done with this class of compounds there appears to be a conspicuous lack of agreement concerning their structure. Of the several formulas proposed, the following have merited the largest consideration.



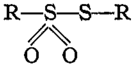
$$R-\underset{\underset{O}{\|}}{S}-\underset{\underset{O}{\|}}{S}-R$$

I



$$R-\underset{\underset{O}{\|}}{S}-O-S-R$$

II



III

The first is the disulfoxide structure; the second is the anhydride structure, and represents the compound as a mixed anhydride of a sulfinic (RSO_2H) and a sulfenic (RSOH) acid; the third is the thiosulfonic ester structure, and relates the compounds to thiosulfonic acids (RSO_2SH).

In a recent paper by Smiles and Gibson,[2] an excellent summary with ample literature references presents the essential arguments for and against each of the three formulas. Concerning the anhydride structure (II), they remark that it "seems to have been based on somewhat ambiguous evidence and has little to be said in its favor, while the arguments against it. . .seem insuperable." Otto and co-workers[3] have shown that the supposed disulfoxides when treated with a mercaptan (or its salt) give a sulfinic acid (or its salt) and a disulfide (R—S—S—R). Smiles and Gibson[2] used this reaction to show in a rather convincing manner that the unsymmetrical or thiosulfonic ester formula (III) is to be preferred to the symmetrical or disulfoxide formula (I). Starting with disulfoxides having like R groups and using mercaptans containing a group R′ different from that in the disulfoxide, they got a mixed disulfide (R—S—S—R′) with a sulfinic acid containing the R group of the disulfoxide. The sulfinic acid corresponding to the mercaptan used was not detected in any of their reaction products.

Their proof is sufficiently conclusive to indicate the incorrectness of the disulfoxide structure. However, it has one weakness. To those who might be inclined to retain the anhydride structure, there appears little in this new work of Smiles and Gibson to militate against such a struc-

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[1] An abstract of this work was presented at the 67th Meeting of the American Chemical Society, Washington, D. C., April 23, 1924.

[2] Smiles and Gibson, *J. Chem. Soc.*, **125**, 176 (1924).

[3] (a) Schiller and Otto, *Ber.*, **9**, 1636 (1876). (b) Pauly and Otto, *Ber.*, **10**, 2184 (1877); (c) **11**, 2071 (1878).

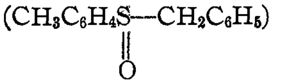
ture. The reaction with mercaptans or their salts can apparently be used with equal effectiveness for the support of the anhydride structure or the thiosulfonic ester structure.

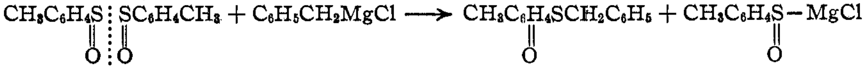
The present work was undertaken in connection with studies concerned with the introduction of R groups by means of the reaction between sulfonic esters and organomagnesium halides.[4] With this as a primary object, the earlier reactions in this study were carried out under so-called forced conditions to determine with certainty whether an R group could be introduced. Some of the products so obtained can be explained on a reasonable basis by accepting the disulfoxide structure. However, when these experiments were repeated later under other conditions, the products were such as to lend themselves to a correct interpretation on the basis of either the anhydride or thiosulfonic ester structures, but not on the disulfoxide structure.

Apparently then, the reaction has only the same limited value as the work of Smiles and Gibson; that is, it serves to show the incorrectness of the disulfoxide structure without deciding definitely between the anhydride or the thiosulfonic ester structures. However, some results of related work on organomagnesium halides, now in progress in this Laboratory, point rather definitely to the validity of the thiosulfonic ester structure, and so confirm the conclusions of Smiles and Gibson on the incorrectness of both the anhydride and the disulfoxide structures.

Interpretation of Reactions

Grignard Reagents and Disulfoxides.—In the earlier experiments, di-*p*-tolyl disulfoxide ($CH_3C_6H_4S_2O_2C_6H_4CH_3$) was added to 1.5 equivalent of benzylmagnesium chloride. The reaction mixture, with ether as a solvent, was refluxed for one hour. After the mixture had been hydrolyzed with dil. sulfuric acid, it was subjected to steam distillation. The sole products obtained from this run (and from another where 2.5 equivalents of benzylmagnesium chloride were used) were *p*-tolyl-benzyl sulfoxide ($CH_3C_6H_4\underset{\underset{O}{\|}}{S}—CH_2C_6H_5$) and *p*-toluenesulfonic acid. Without considering the possibility of intermediate addition to an S=O group, the products so obtained appear to be explained best according to Formula I, as follows.





$$CH_3C_6H_4\underset{\underset{O}{\|}}{S}\,\vdots\,\underset{\underset{O}{\|}}{S}C_6H_4CH_3 + C_6H_5CH_2MgCl \longrightarrow CH_3C_6H_4\underset{\underset{O}{\|}}{S}CH_2C_6H_5 + CH_3C_6H_4\underset{\underset{O}{\|}}{S}-MgCl$$

The hypothetical *p*-toluenesulfenic acid obtained by hydrolysis can probably be converted by oxidation and further hydrolysis to the corresponding sulfonic acid.[5]

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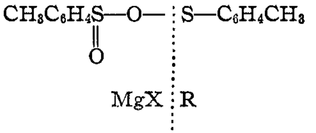
[4] (a) Gilman and Hoyle, THIS JOURNAL, **44**, 2621, 2969 (1922). (b) Gilman and Beaber, *ibid.*, **45**, 839 (1923); (c) **47**, 518 (1925).

Fromm, *Ber.*, **41**, 3397 (1908). Fromm and Siebert, *Ber.*, **55**, 1014 (1922).

However, subsequent experiments with the same reagents demonstrated the incorrectness of such an interpretation. Using equivalent quantities of disulfoxide and benzylmagnesium chloride, and omitting the one-hour period of refluxing subsequent to addition as well as the steam distillation, the products obtained were some unchanged disulfoxide, a small quantity of *p*-tolyl-benzyl sulfoxide, a large amount of *p*-toluenesulfinic acid, and *p*-tolyl-benzyl sulfide ($CH_3C_6H_4SCH_2C_6H_5$). Because earlier work in this Laboratory showed that sulfoxides could be obtained from sulfinic acids or their salts and RMgX compounds, the next experiments were carried out in a way to avoid this side reaction. This was done by adding one equivalent of benzylmagnesium chloride to an ether solution of the disulfoxide which was refluxed during the addition. The vigorous but smooth reaction gave but two products: *p*-tolyl-benzyl sulfide and *p*-toluenesulfinic acid.

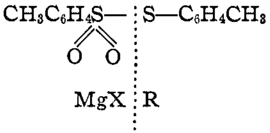
In all other reactions between disulfoxide and various RMgX compounds no sulfoxide was obtained. The sulfide resulting from these reactions contained the R group of the Grignard reagent and the *p*-tolyl group of the disulfoxide. The other product was either *p*-toluenesulfinic acid when the ether layer of the hydrolyzed reaction mixture was extracted with dilute alkali or the corresponding sulfonic acid when steam distillation was used.

The formation of sulfide and sulfinic acid can be explained by either Structure II or III in the following manner, if we again omit consideration of the possible intermediate addition to an S═O group.



$$\begin{array}{l} CH_3C_6H_4\underset{\underset{\displaystyle O}{\|}}{S}—O—\,\vdots\,S—C_6H_4CH_3 \\ \qquad\qquad\quad MgX\,\vdots\,R \end{array}$$

A



$$\begin{array}{l} CH_3C_6H_4\underset{O\;\;O}{S}—\,\vdots\,S—C_6H_4CH_3 \\ \qquad\qquad MgX\,\vdots\,R \end{array}$$

B

Admittedly, there is a possibility that even Formula I may account for the sulfide and sulfinic acid. This would involve a preliminary cleavage between the two sulfur atoms to give a sulfoxide and the bromomagnesium salt of *p*-toluenesulfenic acid ($CH_3C_6H_4S—O—MgBr$). The hypothetical *p*-toluenesulfenic acid could then undergo oxidation to the corresponding sulfinic acid. However, to account for the sulfide one would have to assume reduction of the sulfoxide by the RMgX compound. Some Grignard reagents effect reductions, and under decidedly forced conditions it is possible to reduce a sulfoxide to a sulfide.[6] Such reduction did not take place, under the conditions of study used, for an ether solution of *p*-tolyl-benzyl sulfoxide when refluxed with four equivalents of benzylmagnesium chloride for one hour gave no sulfide.

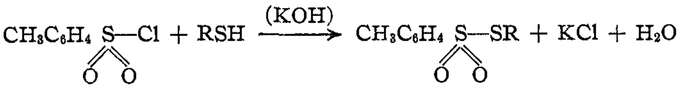
[6] Hepworth and Clapham, *J. Chem. Soc.*, **119**, 1188 (1921).

It was hoped that a decision could be made between mechanisms A and B presented above, by treating the reaction mixture prior to hydrolysis with some reagent which would indicate the mode of attachment of the —MgX group. Earlier successful work with diethyl sulfate suggested this reagent.[4a] However, when the reaction mixture from the disulfoxide and phenylmagnesium bromide was refluxed with diethyl sulfate and then hydrolyzed, no evidence of the ethyl sulfinic ester (from A) or the ethyl sulfone (from B) was obtained. It is known that an —MgX attached to oxygen is replaced with difficulty by an ethyl group.[4b,7] Furthermore, work now in progress shows that an —MgX group attached to sulfur holding two oxygens (see B) takes part in practically no replacement reactions other than those induced by hydrolysis.

On the basis of this work, therefore, it is impossible to decide at present between the anhydride and the thiosulfonic ester formulas. However, some results of other studies point very strongly to the correctness of the ester structure.

Sulfochloride and Mercaptans.—First, it has been known for a long time that the thiosulfonic esters cannot be prepared by the interaction of a sulfochloride and a mercaptan or its salt.[3] The related sulfonic esters can be made by using a sulfochloride and an alcohol or phenol (or their salts). In view of some recent work concerned with the preparation of sulfonic esters in improved yields, this method of synthesis was tried here, particularly because it was found possible to prepare new sulfonic esters which could not be prepared by earlier methods.[4c] This improved method of Hahn and Walter[8] involves the interaction of sulfochloride, alcohol and solid potassium hydroxide in a dry ether solution which is not allowed to rise over 4°.

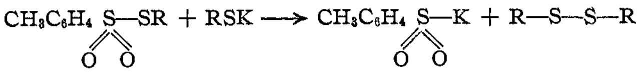
When this method was used in an attempt to synthesize the thiosulfonic esters, the same type of products was obtained as described by earlier investigators; namely, a disulfide and a sulfinic acid. By analogy with the formation of sulfonic esters, it appears highly probable that a thiosulfonic ester was formed as an intermediate compound.



$$CH_3C_6H_4\underset{O\ \ O}{S}-Cl + RSH \xrightarrow{(KOH)} CH_3C_6H_4\underset{O\ \ O}{S}-SR + KCl + H_2O$$

(1)

The ester then underwent reaction, in the known manner, with unaltered mercaptan or its salt to give the disulfide and *p*-toluenesulfinic acid (or its potassium salt).



$$CH_3C_6H_4\underset{O\ \ O}{S}-SR + RSK \longrightarrow CH_3C_6H_4\underset{O\ \ O}{S}-K + R-S-S-R$$

(2)

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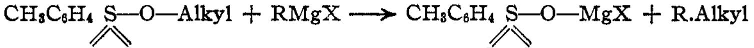
[7] Gilman and Kinney, THIS JOURNAL, **46,** 493 (1924).

[8] Hahn and Walter, *Ber.*, **54B,** 1531 (1921).

Reaction 2 takes place very smoothly under the conditions of this experiment, for when di-*p*-tolyl disulfoxide (prepared according to known methods) was treated with potassium hydroxide and thiocresol in dry ether at 0° an excellent yield of di-*p*-tolyl disulfide was obtained.

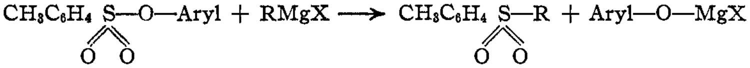
If we admit, as one must, the presence of an $-\underset{\substack{\diagup\diagdown\\ O\quad O}}{S}-$ group in *p*-toluenesulfochloride, and then consider the unusually mild conditions of the experiment (dry ether and 0°), as well as the fact that sulfonic esters (having an $-\underset{\substack{\diagup\diagdown\\ O\quad O}}{S}-$ group) are readily prepared by the same reaction if an alcohol is substituted for the related analogous mercaptan, then it appears highly reasonable that the so-called disulfoxides have the $-\underset{\substack{\diagup\diagdown\\ O\quad O}}{S}-$ group. Only the thiosulfonic ester formula (III) contains such a group.

***p*-Thiocresylmagnesium Iodide and Esters.**—Second, that the $-\underset{\substack{\diagup\diagdown\\ O\quad O}}{S}-$ grouping is present in thiosulfonic esters finds additional supporting evidence in other reactions involving compounds known to have the $-\underset{\substack{\diagup\diagdown\\ O\quad O}}{S}-$ group. When alkyl esters of aryl sulfonic acids are treated with RMgX compounds, the following reaction takes place.[4b,4c]



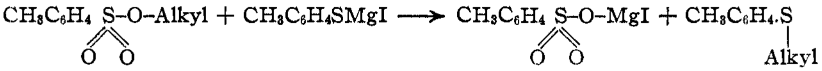
$$CH_3C_6H_4\underset{\substack{\diagup\diagdown\\ O\quad O}}{S}-O-Alkyl + RMgX \longrightarrow CH_3C_6H_4\underset{\substack{\diagup\diagdown\\ O\quad O}}{S}-O-MgX + R.Alkyl \quad (3)$$

With aryl esters a sulfone and phenol are formed.



$$CH_3C_6H_4\underset{\substack{\diagup\diagdown\\ O\quad O}}{S}-O-Aryl + RMgX \longrightarrow CH_3C_6H_4\underset{\substack{\diagup\diagdown\\ O\quad O}}{S}-R + Aryl-O-MgX \quad (4)$$

In connection with studies concerned with the —SMgX linkage,[9] it has been shown that compounds such as *p*-thiocresylmagnesium iodide ($CH_3C_6H_4SMgI$) behave towards carboxylic esters in a manner identical with Grignard reagents having the —MgX group attached to carbon, as in *p*-tolylmagnesium iodide. For this reason, *p*-thiocresylmagnesium iodide was treated with sulfonic esters to see whether the thiosulfonic ester could be prepared. The reaction with alkyl esters of *p*-toluenesulfonic ester went exactly as one might have predicted—an alkyl group was introduced, as is the case with all —CMgX compounds studied.



$$CH_3C_6H_4\underset{\substack{\diagup\diagdown\\ O\quad O}}{S}-O-Alkyl + CH_3C_6H_4SMgI \longrightarrow CH_3C_6H_4\underset{\substack{\diagup\diagdown\\ O\quad O}}{S}-O-MgI + CH_3C_6H_4.\underset{\substack{|\\ Alkyl}}{S} \quad (5)$$

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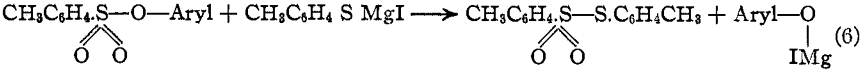
[9] Unpublished work of Mr. W. B. King.

With aryl esters of sulfonic acids we should expect to get, as intermediate compounds, the thiosulfonic ester and phenol, as follows.

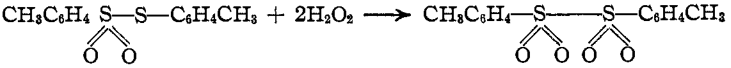


$$\mathrm{CH_3C_6H_4.\underset{O\ \ O}{S}-O-Aryl + CH_3C_6H_4\,S\,MgI \longrightarrow CH_3C_6H_4.\underset{O\ \ O}{S}-S.C_6H_4CH_3 + Aryl-\underset{IMg}{\underset{|}{O}}} \qquad (6)$$

The compounds actually obtained from this reaction, in addition to the phenol, were di-*p*-tolyl disulfide and *p*-toluenesulfinic acid. The formation of the latter two compounds was undoubtedly due to the interaction between the first formed thiosulfonic ester and *p*-thiocresylmagnesium iodide. This course of the reaction is again as would have been predicted, for the *p*-thiocresylmagnesium iodide is a salt of an RSH compound and would accordingly be expected to behave according to Reaction 2. Confirmation of this point was secured by treating the supposed disulfoxide, prepared by known methods, with *p*-thiocresylmagnesium iodide under the conditions used in the reaction with the aryl ester of *p*-toluenesulfonic acid. Di-*p*-tolyl disulfide and *p*-toluenesulfinic acid were obtained.

Here, again, we are concerned with reactions of compounds, the sulfonic esters, known to have the $-\underset{O\ \ O}{S}-$ group. Furthermore, the analogies are virtually complete: *p*-thiocresylmagnesium iodide behaves toward carboxylic esters, alkyl and *aryl*, like the corresponding RMgX compounds when —MgX is attached to carbon; it reacts with alkyl esters of aromatic sulfonic acids like the corresponding RMgX compounds (see Reactions 3 and 5), and there is no apparent reason why the analogy should break down in the reaction with aryl esters of aromatic sulfonic acids (see Reactions 4 and 6). That it does not break down is indicated, at least, in the experiment with the disulfoxide and *p*-thiocresylmagnesium iodide. It is difficult to interpret the several reactions of *p*-thiocresylmagnesium iodide on the basis of any structure other than that of the thiosulfonic ester (III).

Oxidation of Disulfoxide.—Third, when the supposed disulfoxide is allowed to stand at room temperature in a solution of acetic anhydride to which 30% hydrogen peroxide has been added, two atoms of oxygen are added, and the known di-*p*-tolyl disulfone is formed. The reaction may be formulated as follows.



$$\mathrm{CH_3C_6H_4\,\underset{O\ \ O}{S}-S-C_6H_4CH_3 + 2H_2O_2 \longrightarrow CH_3C_6H_4-\underset{O\ \ O}{S}-\underset{O\ \ O}{S}-C_6H_4CH_3}$$

The objection may be raised that the thiosulfonic ester was first hydrolyzed to sulfenic and sulfinic acids which were then oxidized to the α-disulfone. However, a parallel experiment in which the hydrogen peroxide was replaced by an equal weight of water, showed that the compound underwent no hydrolysis.

If we accept the structure of the α-disulfones, as all workers with these compounds have done,[10] and if we admit that the possibility of hydrolysis under the conditions is rather remote, then we have in this experiment additional confirmatory evidence for the thiosulfonic ester structure. Admittedly, the disulfoxide structure also finds support in this oxidation reaction. However, all the other work presented here with that of Smiles and Gibson[2] restricts the choice of a correct formula to those of the anhydride and thiosulfonic ester structures, and the anhydride structure cannot apparently explain the oxidation to disulfone.

Wedekind and Schenck[11] in a study of the reaction between sulfochlorides and the Grignard reagent, obtained small yields of di-*p*-tolyl disulfoxide from *p*-toluenesulfochloride and methylmagnesium iodide and ethylmagnesium bromide. If one admits the possibility of reducing the sulfochloride to the corresponding *p*-thiocresol under the conditions of their experiments, then the *p*-thiocresylmagnesium halide should react with sulfochloride to give the disulfoxide. However, any excess of RMgX compound should react with the disulfoxide if the ether solution was refluxed. In their experiments the solutions were cooled because of the vigor of the reaction.

Experimental Part

Di-*p*-Tolyl Disulfoxide and the Grignard Reagents. Benzylmagnesium Chloride.—A solution of 41.7 g. or 0.1 mole of di-*p*-tolyl disulfoxide[12] in ether was added to about 0.15 mole of benzylmagnesium chloride while the mixture was stirred. A reaction occurred at once as was evidenced by the evolution of heat and the formation of a turbid solution which finally became semi-solid. After the mixture had been refluxed for one hour it was allowed to stand overnight and then was hydrolyzed by cold, 5% sulfuric acid. The oily residue after steam distillation of the ether layer gave 9 g. or a 39% yield of *p*-tolyl-benzyl sulfoxide. Two other compounds were obtained in small amounts and were not identified. One of them contained sulfur and was a white, crystalline solid melting[13] at 183–184°. The quantity of this compound was 1.5 g.

The other compound, 2 g. of which was obtained, melted at 90–92° and contained no sulfur. From the aqueous solution after steam distillation 9 g. was obtained, or a 37% yield of *p*-toluenesulfonic acid.

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[10] Kohler and MacDonald, *Am. Chem. J.*, **22**, 219 (1899). Smiles and Hilditch, *J. Chem. Soc.*, **91**, 519 (1907). Hilditch, *ibid.*, **93**, 1524 (1908).

A later paper will contain an account of the reactions of organomagnesium halides with disulfones, ketosulfones and the anhydrides of various sulfur acids.

[11] Wedekind and Schenck, *Ber.*, **54B**, 1604 (1921). See also Hepworth and Clapham, *J. Chem. Soc.*, **119**, 1188 (1921).

[12] The di-*p*-tolyl disulfoxide was prepared by two standard methods. The method of Otto [*Ann.*, **145**, 318 (1868)] gave a yield of 70%. The method of Hilditch [*J. Chem. Soc.*, **97**, 1098 (1910)] gave a yield of 33%. However, but one run was made by the latter method, and it is quite probable that it is the superior method. Gibson and Smiles[2] prepared a number of disulfoxides by the method of Hilditch and found it better than any other method.

[13] The temperatures recorded in this paper are uncorrected.

Another run made under like conditions but using 2.5 equivalents of benzylmagnesium chloride yielded 41% of *p*-tolyl-benzyl sulfoxide.

In a third experiment, 27.8 g. or 0.1 mole of the disulfoxide was added to an equivalent amount of benzylmagnesium chloride kept cold by an ice-salt mixture. After the mixture had been stirred for two hours at room temperature, it was hydrolyzed as before. An extract of the ether layer in 10% sodium hydroxide solution gave 5.6 g. or a 35.8% yield of *p*-toluenesulfinic acid. After a small amount of unchanged disulfoxide had crystallized from the remaining concentrated ethereal solution, an oil separated. When subjected to steam distillation this oil gave 1.5 g. or a 7% yield of *p*-tolyl-benzyl sulfide and 2 g. or a 9% yield of *p*-tolyl-benzyl sulfoxide.

When the order of addition was reversed and the benzyl-magnesium chloride added to a refluxed ether solution containing 15 g. of the disulfoxide, no *p*-tolyl-benzyl sulfoxide was obtained. The alkaline extract of the ether solution after hydrolysis gave 8.5 g., or an approximate 100% yield, of *p*-toluenesulfinic acid. The ether solution, when evaporated, yielded 2.6 g. or 22.5% of *p*-tolyl-benzyl sulfide.

To account for the formation of *p*-tolyl-benzyl sulfoxide in the earlier experiments, a mixture of 0.11 mole of benzyl-magnesium chloride and 0.039 mole of *p*-toluenesulfinic acid was refluxed in ether for one hour. The reaction product, when worked up in the customary manner, gave 23.1% of *p*-tolyl-benzyl sulfoxide and 56.7% of unaltered *p*-toluenesulfinic acid.

Phenylmagnesium Bromide.—A solution of 27.8 g. or 0.1 mole of the disulfoxide at room temperature in 0.11 mole of phenylmagnesium bromide was refluxed for one hour. In addition to about 1 g. of unchanged disulfoxide, there were obtained 5.3 g. or a 34% yield of *p*-toluenesulfinic acid and 4 g. or a 20% yield of *p*-tolyl-phenyl sulfide.

In another run, after refluxing had been continued for two hours, 1.3 equivalent, of diethyl sulfate was added and the mixture was then refluxed for one hour prior to hydrolysis. In addition to a 54% yield of *p*-toluenesulfinic acid and a 69% yield of *p*-tolyl-phenyl sulfide, about 0.4 g. of an unidentified compound melting at 100° was obtained. Apparently, neither ethyl *p*-toluenesulfinate nor ethyl *p*-tolyl sulfone was present.

***p*-Tolylmagnesium Bromide.**—From a reaction between 0.1 mole of the disulfoxide and 0.25 mole of *p*-tolylmagnesium bromide there were obtained a 65% yield of di-*p*-tolyl sulfide and a 51% yield of *p*-toluenesulfonic acid. As in the first experiments with benzyl-magnesium chloride, the sulfonic acid was recovered after steam distillation, and the yield reported is less than that actually obtained because some material was lost by decomposition in a preliminary separation by vacuum distillation.

Methylmagnesium Iodide.—From 15 g. or 0.054 mole of the disulfoxide and 0.12 mole of methylmagnesium iodide was obtained 6.5 g. or an 87% yield of *p*-tolyl-methyl sulfide. The sulfonic acid was not worked up.

Ethyl *p*-Toluenethiosulfonate ($CH_3C_6H_4S_2O_2C_2H_5$) and Phenylmagnesium Bromide.[14]—An ether solution containing 16.2 g., 0.075 mole, of ethyl *p*-toluenethiosulfonate[15] was added slowly, with stirring, to 0.15 mole of phenylmagnesium bromide. The reaction was decidedly vigorous, and after refluxing had been continued for five hours the mixture was allowed to stand overnight. The clear ether solution was then decanted, treated with cold dil. sulfuric acid, washed with water and dried by potassium carbonate. Vacuum distillation gave 3 g. or a 29% yield of phenyl-ethyl sulfide. As was the case with practically all sulfides and sulfoxides obtained in this study, its identifi-

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[14] The experiments under this and the following two headings were performed by Nathaniel J. Beaber.

[15] The ethyl *p*-toluenethiosulfonate was prepared by the method of Otto, *Ber.* **15,** 121 (1882).

cation was completed by oxidizing with 30% hydrogen peroxide to the corresponding sulfone, and then making a mixed-melting-point determination.

A special search was made for ethyl benzene, but none was found.[16]

_p_-Toluenesulfochloride with _p_-Thiocresol and _n_-Butyl Mercaptan.—To 38 g. (0.2 mole) of _p_-toluenesulfochloride dissolved in 200 cc. of anhydrous ether were added slowly in small portions, 30 g. or 0.54 mole of freshly powdered potassium hydroxide and 24.8 g. or 0.2 mole of _p_-thiocresol, the addition being so regulated that potassium hydroxide was always in excess. After the mixture had been stirred for four hours at the same low temperature that was maintained during the addition (—2° to —6°), it was poured into ice water. The ether layer was extracted with dil. sodium hydroxide solution to insure complete removal of any unchanged thiocresol, and then dried over calcium chloride; yield of di-_p_-tolyl disulfide 21.5 g., or 87.4%. As was the case with all other disulfides obtained in this study, its identity was confirmed by a mixed-melting-point determination.

A similar reaction between 53.2 g. or 0.28 mole of _p_-toluene-sulfochloride and 25 g. or 0.28 mole of _n_-butyl mercaptan gave 11.6 g. or a 46.6% yield of di-_n_-butyl disulfide; b. p., 110–113° (15 mm.); n^{22}_{D}, 1.494; d^{20}_{4}, 0.930. To confirm the identity of this substance some of it was prepared by the method of Kekulé and Linnemann[17] from _n_-butyl mercaptan, sodium hydroxide and iodine. The physical constants of the two compounds agreed.

Di-_p_-tolyl Disulfoxide and _p_-Thiocresol.—The reaction between 5.6 g. (0.02 mole) of di-_p_-tolyl disulfoxide, 2.5 g. (0.02 mole) of _p_-thiocresol and 3 g. (0.05 mole) of powdered potassium hydroxide was carried out under exactly the conditions described in the reaction between _p_-toluene-sulfochloride and _p_-thiocresol; yield of di-_p_-tolyl disulfide, 4.6 g., or 78%.

Ethyl and Phenyl Benzoates with _p_-Thiocresylmagnesium Iodide.[18]—To 0.3 mole of _p_-thiocresylmagnesium iodide was added 45 g. or 0.3 mole of ethyl benzoate. Gentle refluxing soon commenced and the solution became light red. The color deepened very considerably during an 18-hour period of refluxing. After hydrolysis with dil. hydrochloric acid, the ether layer was washed with dil. alkali to remove unaltered thiocresol and then dried by sodium sulfate. Vacuum distillation of the oil remaining after the removal of ether gave 31 g. of unchanged ethyl benzoate and 12 g. of _p_-tolyl thiolbenzoate ($C_6H_5C(O)SC_6H_4CH_3$).

In a corresponding experiment, 25 g. or 0.125 mole of phenyl benzoate was refluxed for 12 hours with an ether solution of 0.125 mole of _p_-thiocresylmagnesium iodide; 18 g. or a 71% yield of _p_-tolyl thiolbenzoate was obtained in addition to 4 g. of unchanged _p_-thiocresol. As in the experiment with ethyl benzoate, the _p_-tolyl thiolbenzoate was confirmed by a mixed-melting-point determination.

Ethyl and Phenyl _p_-Toluenesulfonates with _p_-Thiocresylmagnesium Iodide.—Forty g. or 0.2 mole of ethyl _p_-toluenesulfonate was added to an ether solution containing 0.2 mole of _p_-thiocresylmagnesium iodide. A vigorous reaction took place and a characteristic[4] thickening of the solution was noted after a five-hour period of refluxing. After the mixture had been treated in the customary manner, 18 g., or 65.5% yield of _p_-tolyl-ethyl sulfide was obtained in addition to 5 g. of unaltered _p_-thiocresol.

A mixture of 49.6 g. or 0.2 mole of phenyl _p_-toluenesulfonate and an ether-toluene[19]

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[16] This was done in order to determine whether the alkyl esters of thiosulfonic acids can alkylate according to the known reactions of the corresponding sulfonic esters.[4b,c]

[17] Kekulé and Linnemann, _Ann._, **123**, 273 (1852).

[18] The experiments under this and the following two headings were performed by W. Bernard King.

[19] Toluene was used here because in the study of aryl esters of _p_-toluenesulfonic

solution containing 0.2 mole of *p*-thiocresylmagnesium iodide was refluxed for 12 hours. After the product had been treated in the customary manner, 10 g. or a 20.3% yield of di-*p*-tolyl disulfide was separated from 38 g. of unaltered phenyl *p*-toluenesulfonate by extraction with petroleum ether.

Di-*p*-Tolyl Disulfoxide and *p*-Thiocresylmagnesium Iodide.—A mixture of 2.2 g. or 0.008 mole of di-*p*-tolyl disulfoxide with an ether-toluene solution containing 0.008 mole of *p*-thiocresylmagnesium iodide was refluxed for eight hours. The mixture was treated in a manner identical with that from the reaction between phenyl *p*-toluenesulfonate and *p*-thiocresylmagnesium iodide: yield of di-*p*-tolyl disulfide, 1.2 g., or 61%.

Di-*p*-Tolyl Disulfoxide and Hydrogen Peroxide.[20]—To a solution of 2 g. of di-*p*-tolyl disulfoxide in a mixture of acetic anhydride and acetic acid was added 3 g. of 30% hydrogen peroxide. The acetic anhydride was in excess of that required to react with the water in the peroxide solution, and sufficient acetic acid was added to keep the disulfoxide in solution. After the mixture had stood for two days at room temperature, crystals began to form and these had increased slightly in quantity at the end of six days. They were separated by decantation, and a mixed-melting-point determination with the known di-*p*-tolyl disulfone showed no depression.

These results were duplicated in an experiment made under similar conditions.

When 5 g. of the disulfoxide was allowed to stand for two weeks at room temperature with 6 g. of water, 40 g. of acetic anhydride and sufficient acetic acid to keep the compound in solution, no change was noted. Practically all (over 90%) of the disulfoxide was recovered by pouring the solution into water.

Summary

The reactions of the so-called disulfoxides with organomagnesium halides and hydrogen peroxide show that the thiosulfonic ester structure is to be preferred to the disulfoxide and the anhydride formulas.

AMES, IOWA

[CONTRIBUTION FROM THE LABORATORY OF THE J. B. WILLIAMS COMPANY]

A METHOD FOR THE PREPARATION OF PRIMARY ACETYLENIC ALCOHOLS

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The only method described in the literature for the preparation of alcohols of the type $R.C{\vdots}C.CH_2OH$ is that of Moureu and Desmots[1] which depends upon the action of dry trioxymethylene on the sodium derivatives of the acetylenes. This method, according to the authors' own testimony, is very unsatisfactory, yielding only a small percentage of the desired product and producing as a by-product a high-boiling alcohol of the formula $C_{16}H_{26}O$.

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acid and RMgX compounds it was found desirable to use a higher temperature than that used with alkyl esters. A preliminary report of this work has already been made, (Ref. 4 c) and the final report will be contained in a paper to be published shortly.

[20] The experiments under this heading were performed by Chester E. Adams.

[1] Moureu and Desmots, *Bull. soc. chim.*, [3] **27**, 360 (1902).