Summary

1. Alkali metal alkyls react with quaternary phosphonium halides at room temperature.

2. Tetra-ethylphosphonium iodide and sodium triphenylmethyl give at once colorless products and the reaction is apparently analogous to that between alkali metal alkyls and quaternary ammonium salts.

3. Triphenylalkylphosphonium halides react with alkali metal alkyls to give colored products, apparently identical with the phosphinemethylenes of Staudinger, as the primary products of the reaction. The products isolated from several different reactions of this type are easily explained as decomposition products of the intermediate phosphinemethylenes.

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THE REACTION BETWEEN SULFOCHLORIDES AND ORGANOMAGNESIUM HALIDES

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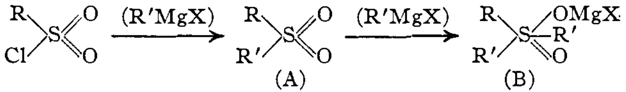
Introduction

In connection with studies on the electronic interpretation of the ethylenic linkage, Gilman and Peterson[1] reported a complete reaction between ethylmagnesium bromide and di-*p*-tolyldisulfonethylene. In order to throw some light on the nature of that reaction it was advisable to study a simpler conjugated system of the same type, namely, styryl-*p*-tolylsulfone ($p\text{-}CH_3C_6H_4\underset{O\quad O}{\underset{\diagup\!\diagdown}{S}}—CH{=}CHC_6H_5$). With this in view, we set out to prepare the sulfone from *p*-toluenesulfochloride and styrylmagnesium bromide. The indifferent success attending this synthesis prompted a more general investigation of the reaction between sulfochlorides and RMgX compounds.

Earlier studies of this reaction were made by Hepworth and Clapham[2] and by Wedekind and Schenk.[3] Hepworth and Clapham[2] proposed the following reactions to account for the sulfones ($R—\underset{O\quad O}{\underset{\diagup\!\diagdown}{S}}—R$), sulfoxides ($R—\overset{O}{\overset{\diagup\!\!\diagup}{S}}—R$) and sulfides (R—S—R) isolated by them from the reaction between benzenesulfochloride and some RMgX compounds.



(I)

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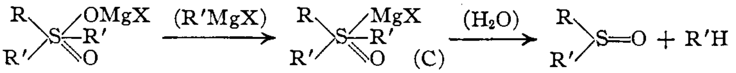
[1] Gilman and Peterson, THIS JOURNAL, **48**, 423 (1926).

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

[3] Wedekind and Schenk, *Ber.*, **54**, 1604 (1921).

Compound B may then react further with R'MgX, as follows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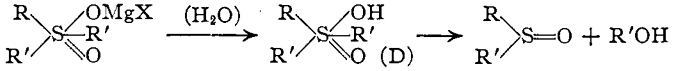
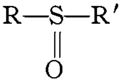
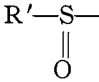
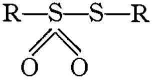
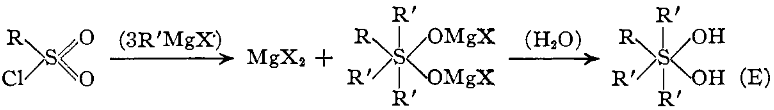

(III)

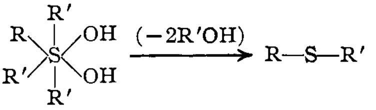
They explained the formation of sulfides by the further action of organomagnesium halide on Compounds B and C.

There are several objections to these reactions. First, an R'Cl compound is formed, the R' coming from the R'MgX and the Cl from the sulfochloride. Apparently they did not observe the formation of the chloride. Second, it is very doubtful if the intermediate compounds B, C and D are formed. Were such compounds formed, then it is reasonable to suppose that from Compound C, for example, one should get a mixture of sulfoxides,  $\mathrm{R{-}\underset{O}{\underset{\|}{S}}{-}R'}$ and  $\mathrm{R'{-}\underset{O}{\underset{\|}{S}}{-}R'}$. Actually, such mixtures of sulfoxides have not been reported. Third, the removal of oxygen when Compound B is converted to Compound C by means of an excess of R'MgX compound involves the oxidation of the R'MgX to an alcohol or a phenol; but, as stated by them in connection with their Reaction III, alcohols and phenols were not observed. It is, of course, possible that the atom of oxygen might be removed by two additional molecules of RMgX to give R·R and $(MgX)_2O$. This, however, has the objection of requiring a larger quantity of R·R than that actually found.

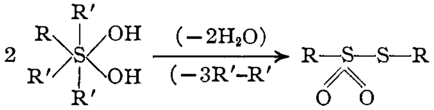
Wedekind and Schenk[3] proposed the following reactions to account for the same compounds isolated by Hepworth and Clapham,[2] in addition to the thiosulfonic ester,  $\mathrm{R{-}\underset{O\;\;O}{S}{-}S{-}R}$, they obtained.


(IV)

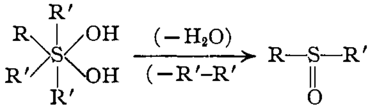
The formation of sulfide was explained by the removal of two molecules of R'OH, as follows


(V)

They explained the formation of the thiosulfonic ester by the removal of two molecules of water and three molecules of an R'-R' compound from two molecules of Compound E, as follows:


(VI)

Finally, they proposed the following reaction for the formation of sulfoxide


(VII)

There are also several objections to these reactions proposed by Wedekind and Schenk.[3] First, they make no mention of the formation of R′Cl compound. Second, the thiosulfonic esters are only what might be termed accidental reaction products; that is, the thiosulfonic esters only come into the picture of things *after* one of the true reaction products—the sulfinic acids, RSO_2H—are formed. It has long been known that sulfinic acids are readily converted to thiosulfonic esters.[4] Actually, we have shown that only sulfinic acid is obtained when the reaction products are worked up promptly, and that thiosulfonic esters and not sulfinic acids are obtained when the solutions containing sulfinic acids are allowed to stand for an appreciable time. Third, it seems reasonable to expect that Reaction V should give rise to a mixture of sulfides, namely, R—S—R′ and R′—S—R′. Fourth, it seems equally reasonable to expect that Reaction VI should lead to a mixture of thiosulfonic esters, and Reaction VII to a mixture of sulfoxides, $\mathrm{R{-}\underset{\underset{O}{\|}}{S}{-}R'}$ and $\mathrm{R'{-}\underset{\underset{O}{\|}}{S}{-}R'}$. A fifth objection can be raised against Reactions VI and VII. Each of these reactions postulates the formation of R·R compounds. In our studies the quantities of diphenyl and of di-*p*-tolyl are only slightly greater than one would expect of these R·R compounds incidental to the preparation of phenylmagnesium bromide and *p*-tolylmagnesium bromide, respectively. Wedekind and Schenk[3] believed that Reactions VI and VII were reasonable because of the quantity of diphenyl they obtained. Actually, however, the yields of diphenyl reported by them are no greater than those generally obtained in a *careful* preparation of phenylmagnesium bromide.

As usual, it is generally an easier thing to criticize a series of reactions than to propose a series that can withstand criticism. The chief products isolated by us, and under our experimental conditions, were sulfones, sulfinic acids and RX compounds (the R coming from the Grignard reagent and the X from the sulfohalide). In the later more exact experiments, after we were aware of the formation of sulfinic acids and RX com-

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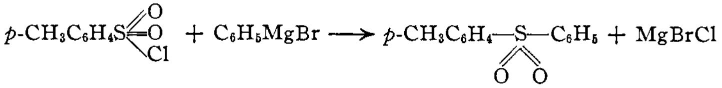
[4] Gilman, Smith and Parker, This Journal, **47**, 851 (1925). This paper, on the constitution of thiosulfonic esters, contains many of the important and leading references to the reactions of sulfinic acids, etc.

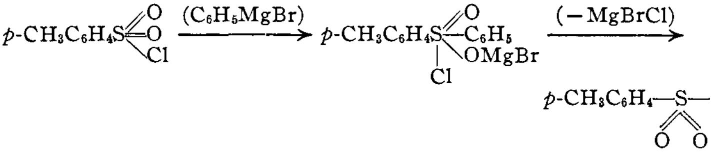
pounds, we observed that these two products were formed in about equivalent quantities.

The most reasonable reaction for the formation of sulfones is a so-called direct substitution, as follows



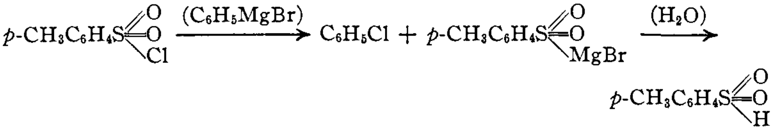
$$p\text{-}CH_3C_6H_4S\begin{smallmatrix}\diagup O\\ = O\\ \diagdown Cl\end{smallmatrix} + C_6H_5MgBr \longrightarrow p\text{-}CH_3C_6H_4\text{—}\underset{\diagup\ \diagdown \atop O\quad O}{S}\text{—}C_6H_5 + MgBrCl \qquad (VIII)$$

Of course, there is the possibility that these products might have resulted subsequent to addition of the Grignard reagent to the sulfonyl group (S=O), as follows



$$p\text{-}CH_3C_6H_4S\begin{smallmatrix}\diagup O\\ = O\\ \diagdown Cl\end{smallmatrix} \xrightarrow{(C_6H_5MgBr)} p\text{-}CH_3C_6H_4\underset{Cl}{\underset{|}{S}}\begin{smallmatrix}\diagup O\\ -C_6H_5\\ \diagdown OMgBr\end{smallmatrix} \xrightarrow{(-MgBrCl)} p\text{-}CH_3C_6H_4\text{—}\underset{\diagup\ \diagdown \atop O\quad O}{S}\text{—}C_6H_5 \qquad (IX)$$

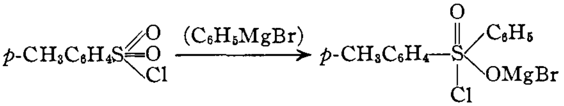
Probably the most acceptable reaction for the formation of sulfinic acid and halide is again a direct substitution (like that of Reaction VIII) but this time the halogen of the sulfohalide is replaced by the $-MgX$ group and not by the R-group of the RMgX compound, as follows



$$p\text{-}CH_3C_6H_4S\begin{smallmatrix}\diagup O\\ = O\\ \diagdown Cl\end{smallmatrix} \xrightarrow{(C_6H_5MgBr)} C_6H_5Cl + p\text{-}CH_3C_6H_4S\begin{smallmatrix}\diagup O\\ = O\\ \diagdown MgBr\end{smallmatrix} \xrightarrow{(H_2O)} p\text{-}CH_3C_6H_4S\begin{smallmatrix}\diagup O\\ = O\\ \diagdown H\end{smallmatrix} \qquad (X)$$

A direct substitution of the kind pictured in Reaction X finds support in reactions between the Grignard reagent and compounds having halogen attached directly to sulfur.[5]

There is an attractiveness to postulating addition of the RMgX compound to a sulfonyl group after the proposals of Hepworth and Clapham,[2] Wedekind and Schenk[3] and Reaction IX. However reasonable such a mode of reaction may appear for the explanation of reactions of sulfochlorides, sulfones and sulfoxides, it is of dubious value in interpreting the formation of sulfinic acid and RX compound. If a reaction of this type occurred



$$p\text{-}CH_3C_6H_4S\begin{smallmatrix}\diagup O\\ = O\\ \diagdown Cl\end{smallmatrix} \xrightarrow{(C_6H_5MgBr)} p\text{-}CH_3C_6H_4\text{—}\overset{O}{\underset{Cl}{\underset{|}{\overset{\|}{S}}}}\begin{smallmatrix}\diagup C_6H_5\\ \diagdown OMgBr\end{smallmatrix} \qquad (XI)$$

(F)

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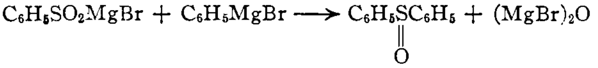
[5] Ferrario, *Bull. soc. chim.*, **7**, 518 (1910), obtained increasing quantities of chlorobenzene from the reaction between sulfur monochloride, dichloride and tetrachloride, respectively, with phenylmagnesium bromide. However, because we have not obtained chlorobenzene from sulfur monochloride, nor from aryl sulfur chlorides (RSCl), and because chlorobenzene is obtained from organic hypochlorites (ROCl) [see Durand and Naves, *ibid.*, **37**, 717 (1925); Gilman and Heckert, *Rec. trav. chim.*, **49**, (1930)] there is a possibility, even though somewhat remote, that sulfochlorides might have a hypochlorite structure, RS(=O)(OCl), in equilibrium with the RSO_2Cl form.

then it appears eminently reasonable that the splitting products should be mixtures of chlorobenzene and *p*-chlorotoluene, and benzenesulfinic acid and *p*-toluenesulfinic acid. Such mixtures were not observed, and the products isolated were chlorobenzene and *p*-toluenesulfinic acid. Furthermore, from benzenesulfochloride and *p*-tolylmagnesium bromide the products were benzenesulfinic acid and *p*-chlorotoluene. This pair of reactions, with the R groups interchanged in the sulfochloride and Grignard reagent, militates against a preliminary addition and indicates a direct substitution.[6]

Our experimental conditions were not those of earlier workers.[2,3] We used equivalent molecular proportions of sulfochloride and Grignard reagent and did not heat the reaction mixtures. However, when we did follow their general directions, we obtained some diphenyl sulfide, a large yield of diphenyl sulfoxide, an equally large yield of chlorobenzene but no sulfinic acid. The absence of sulfinic acid and the high yield of sulfoxide is very probably due to the following reaction[4]



$$C_6H_5SO_2MgBr + C_6H_5MgBr \longrightarrow C_6H_5\underset{\underset{O}{\|}}{S}C_6H_5 + (MgBr)_2O \qquad \text{(XII)}$$

Closely related to the present studies is earlier work by Oddo[7] on sulfuryl chloride (SO_2Cl_2) and by Oddo,[8] Grignard and Zorn,[9] and Strecker[10] on thionyl chloride ($SOCl_2$).

Experimental Part

The reactions were carried out in a three-necked flask provided with a mercury-sealed stirrer, separatory funnel and condenser. The flask containing generally 0.3 mole of sulfochloride in one liter of ether was cooled by an ice-salt mixture. To this was slowly added (three to four hours) the Grignard reagent, and when one molecular equivalent of RMgX compound was added the reaction mixture generally gave the color test described by Gilman, Schulze and Heck.[11] The cold reaction mixture was hydrolyzed with 10% hydrochloric acid, the ether layer separated and then combined with the ether washings of the acid-aqueous layer.

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[6] Of course, we would not be understood to mean that there is no preliminary addition here of a loose type not involving primary or chief valences of the sulfur or oxygen or chlorine or, for that matter, of the magnesium or ether in the Grignard reagent. What we do mean is that a hypothetical compound like Compound F is unreasonable if the phenyl and the *p*-tolyl groups are attached to the sulfur by primary valences. Also, admittedly, the sulfur–carbon linkages holding the phenyl and *p*-tolyl groups would not be, in all probability, of equal strength even though both such linkages were primary. Linkages of slightly different strengths should result, generally, in mixtures having slightly different percentages of components.

[7] Oddo, *Gazz. chim. ital.*, II, **35**, 136 (1905); *Atti accad. Lincei* [5] I, **14**, 169 (1905); see *Chem. Zentr.*, I, 1145 (1905).

[8] Oddo, *Gazz. chim. ital.*, I, **41**, 11 (1911); *C. A.*, **5**, 2635 (1911).

[9] Grignard and Zorn, *Compt. rend.*, **150**, 1177 (1910).

[10] Strecker, *Ber.*, **43**, 1131 (1916).

[11] Gilman and Schulze, This Journal, **47**, 2002 (1925); *Bull. soc. chim.*, **41**, 1479 (1927); Gilman and Heck, *Rec. trav. chim.*, **48**, 193 (1929); *Ber.*, **62**, 1379 (1929).

TABLE I

REACTION BETWEEN SULFOHALIDES AND GRIGNARD REAGENTS

Sulfohalide	Moles	RMgX compound[a]	Sulfone	Yield, %	Sulfinic acid[b] yield, %	RX compound	Yield, %
$C_6H_5SO_2Cl$	0.3	C_6H_5MgBr[c]	$C_6H_5SO_2C_6H_5$	35.0	0.5	C_6H_5Cl	16.3
$C_6H_5SO_2Cl$	.3	p-$CH_3C_6H_4MgBr$[d]	p-$CH_3C_6H_4SO_2C_6H_5$	17.5	46.4	p-$CH_3C_6H_4Cl$	27.0
$C_6H_5SO_2Cl$	.2	α-$C_{10}H_7MgBr$[e]	......	..	..	α-$C_{10}H_7Cl$	39.7
$C_6H_5SO_2Cl$	.3	$C_6H_5CH{=}CHMgBr$[f]	......	..	39.6	$C_6H_5CH{=}CHCl$	40.4
$C_6H_5SO_2Cl$	.3	$C_6H_5C{\equiv}CMgBr$[g]	......	..	1.2	$C_6H_5C{\equiv}CCl$	13.7
$C_6H_5SO_2Cl$	.3	$C_6H_5CH_2MgCl$[h]	$C_6H_5CH_2SO_2C_6H_5$	2.9	..	$C_6H_5CH_2Cl$	60.0
p-$CH_3C_6H_4SO_2Cl$	.3	n-C_4H_9MgBr[i]	......	..	60.6	n-C_4H_9Cl	8.7
p-$CH_3C_6H_4SO_2Cl$	.3	Cyclo-$C_6H_{11}MgBr$[j]	......	..	67.1	Cyclo-$C_6H_{11}Cl$	66.3
p-$CH_3C_6H_4SO_2Cl$	.3	C_6H_5MgBr[k]	p-$CH_3C_6H_4SO_2C_6H_5$	32.9	10.7	C_6H_5Cl	11.0
p-$CH_3C_6H_4SO_2Br$	.1	C_6H_5MgBr[l]	......	..	30.2	C_6H_5Br	53.8
p-$CH_3C_6H_4SO_2I$	.13	C_6H_5MgBr[m]	......	..	11.8	C_6H_5I	65.1
α-$C_{10}H_7SO_2Cl$	.2	C_6H_5MgBr[n]	α-$C_{10}H_7SO_2C_6H_5$	13.0	..	C_6H_5Cl	24.5

[a] Unless otherwise stated, the quantity of RMgX compound used was equivalent to the sulfohalide. That is, with 0.3 mole of sulfohalide, 0.3 mole of RMgX compound was used.

[b] The sulfinic acid obtained was that corresponding with the sulfohalide. For example, with benzenesulfochloride there was obtained benzenesulfinic acid. A search was not always made for the sulfinic acid.

[c] The reactions between benzenesulfochloride and phenylmagnesium bromide were the first studied, and the very small yields of sulfinic acid and chlorobenzene given in Table I were due to an initial unfamiliarity with the course of the reaction. Several experiments were made on the reaction between benzenesulfochloride and phenylmagnesium bromide, and although the yield of diphenylsulfone was consistently around 35%, the yield of chlorobenzene varied between 12.2 and 43.7%. A reaction between these reagents at a temperature below −63° (by solid carbon dioxide and acetone cooling) gave 12.2% of sulfone, 43.7% of chlorobenzene and 6.5% diphenyl, but the sulfinic acid was lost by an attempted vacuum distillation. We had little success in a low temperature reaction so carried out that a mixture of benzenesulfochloride and bromobenzene was added to magnesium and ether.

[d] In addition to the products listed there was obtained 5.2% of di-p-tolyl. No p-cresol was obtained.

[e] A few crystals melting at 97–100° were obtained. These, however, were not the expected α-naphthylphenylsulfone, because of the depression to 70–80° in a mixed melting point determination with an authentic specimen of the sulfone. Unfortunately the alkaline extract that might have contained the sulfinic acid was lost by a mishap.

[f] The yield of diphenylbutadiene from this experiment was 34.2%. We believe that this high yield of R·R compound is due to the extensive coupling reaction incidental to the preparation of β-styrylmagnesium bromide. No sulfone was obtained and inasmuch as the sulfone that might have been expected here was the cause of this study a further investigation is in progress on this reaction. The recovery of a 33.6% yield of styrene (which very probably resulted from hydrolyzed Grignard reagent) is indicative of a lesser reactivity of this RMgX compound toward benzenesulfochloride.

[g] The recovery of phenylacetylene in a 51.2% yield is indicative of a very slow or poor reaction of phenylacetenylmagnesium bromide. This supports other studies now in progress on the relative reactivities of Grignard reagents. However, only 4.5% of the benzenesulfochloride was recovered.

[h] The yield of dibenzyl was 7.7%. In a careful preparation of benzylmagnesium chloride the yield of dibenzyl is 4–5%.

[i] A residue, non-volatile with steam, was obtained. This melted at 68° when recrystallized twice from 95% alcohol. The yield was 13.2 g. and analyses for sulfur by the Carius method gave 17.07 and 17.40% of sulfur. Gilman and Beaber, THIS JOURNAL, **47**, 1449 (1925), reported *n*-butyl-*p*-tolylsulfone as a liquid boiling at 173–175° (3.5 mm.).

[j] A very small quantity (0.2 g.) of a solid melting at 86° was obtained from the residue of the steam distillation.

[k] The yield of diphenyl was 4.5% of that normally obtained incidental to the preparation of phenylmagnesium bromide.

[l] The *p*-toluenesulfobromide and *p*-toluenesulfo-iodide were prepared according to the directions of Whitmore, THIS JOURNAL, **45**, 1069 (1923). The sulfobromide was partially dissolved in 700 cc. of ether and 0.4 mole of phenylmagnesium bromide was required for a positive color test. The reaction flask was cooled by an ice–salt bath, and 20% hydrochloric acid was used in the hydrolysis. The 30.2% yield of *p*-toluenesulfinic acid is based on the yield of *p*-tolyl-*p*-toluenethiosulfonate isolated in this experiment.

[m] The quantity of phenylmagnesium bromide required for a positive color test was 0.7 mole. The initially violent reaction may have been due to some free halogen. No *p*-toluenesulfinic acid was actually isolated and the yield of this compound was based on the *p*-tolyl-*p*-toluenethiosulfonate (see Footnote *l*.)

[n] As in other experiments with phenylmagnesium bromide, the yield of diphenyl was that to be expected from the preparation of phenylmagnesium bromide.

The ether layer, after washing with 5% sodium hydroxide and then with a little water, was steam distilled. The steam distillate was extracted with ether and from the vacuum distillation of this dried ether extract there was obtained the RX and R–R compounds. The residue from steam distillation gave the sulfone.

The alkaline extract was immediately acidified with hydrochloric acid and extracted with ether. This ether solution was then dried by sodium sulfate, and on the rapid removal of the ether by dry air the sulfinic acid was obtained as faintly colored crystals.

The identity of all of the solid reaction products was confirmed by mixed melting point determinations with authentic specimens. The liquid RX compounds were identified by conversion to solid nitro-halogen derivatives, and mixed melting point determinations were then made of these solids with authentic compounds. The results are given in Table I and the footnotes which accompany it.

Benzenesulfochloride and Phenylmagnesium Bromide.—This experiment was carried out under conditions unlike those followed in the runs described in Table I, but like those described by Hepworth and Clapham.[2] During the addition of 53.0 g. (0.3 mole) of benzenesulfochloride in 200 cc. of ether to 0.9 mole of phenylmagnesium bromide solution (450 cc.), the reaction flask was cooled by an ice–salt mixture. When addition was ended, the mixture was allowed to stand at room temperature for seventeen hours and then warmed by a hot plate for one hour. After hydrolysis by dilute hydrochloric acid, the mixture was worked up in the customary manner The following products were obtained: 52.5% of chlorobenzene, 60.2% of diphenyl sulfoxide, 4.1% of diphenyl sulfide, 6.4% of diphenyl, but no benzenesulfinic acid.

Summary

The chief products obtained from the reaction between arylsulfohalides and organomagnesium halides are sulfones, sulfinic acids and RX compounds having the R-group of the RMgX compound and the halogen of the sulfohalide. Previous explanations of this reaction have been corrected and a new interpretation of the reaction has been proposed.

AMES, IOWA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE STANDARD OIL COMPANY OF INDIANA]

TETRAMETHYLETHYLENE SULFIDE

BY MERRILL A. YOUTZ AND PHILIP P. PERKINS

RECEIVED JULY 11, 1929 PUBLISHED NOVEMBER 8, 1929

It is only in comparatively recent years that substances of the type of ethylene sulfide $\overline{CH_2SC}H_2$ have been synthesized. Previous attempts to do so by treating alkylene dibromides with potassium sulfide, etc., have given either a dimer, such as diethylene disulfide or amorphous substances of even higher molecular weights. This is not especially surprising and probably in some cases long chains could be produced by the reaction of each mole of potassium sulfide with two different molecules of $C_2H_4Br_2$. However, the matter is even more involved than this as the recent successful preparation of several of these compounds by Delépine[1] has shown that, even if pure, they polymerize readily. The tendency to polymerize diminishes with increasing molecular weight. His method was to treat a 1,2-dibromide with potassium or ammonium thiocyanate, purify the dithiocyanate and to treat this with dilute sodium sulfide. Especially with the lowest member it was necessary to have the sodium hydrogen sulfide present with the sodium sulfide in order to avoid polymerization during the reaction.

The compounds are readily polymerized by bases or acetic or sulfuric acids. Nitric acid oxidizes them to sulfuric or sulfonic acids. Hydrochloric acid appears to combine forming a chloromercaptan which can be removed with sodium plumbite, etc. Probably the oxidation by nitric

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[1] Delépine, *Compt. rend.*, **171**, 36 (1920); **172**, 158 (1921); *Bull. soc. chim.*, [4] **27**, 740 (1920); **29**, 136 (1921).