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I hereby recommend that the thesis prepared under my supervision by Irving E. Levine

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Approved by:

F E Ray

W. M. Burgess, Chairman

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I. A NEW REACTION MECHANISM FOR ORGANIC HALIDES WITH SULFIDES

II. DERIVATIVES OF 2-FLUORENE-PHENYL-METHANE

A dissertation submitted to the

Graduate School
of the University of Cincinnati

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by

Irving Englander Levine

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I

INTRODUCTION

SULFONIUM COMPOUNDS

In 1864 Oefele (1) reported a "new class of sulfur compounds", the first of which he obtained by warming diethyl sulfide with ethyl iodide in the presence of water. He immediately perceived the analogy between this type of compound and the salts of amines, and accordingly named them "sulfins". In English, however, they are called

$$C_2H_5I + C_2H_5SC_2H_5 \longrightarrow (C_2H_5)_3SI$$

$$C_2H_5I + (C_2H_5)_3N \longrightarrow (C_2H_5)_4NI$$

sulfonium compounds in direct analogy to the ammonium compounds.

Oefele also made triethyl sulfonium iodide by distilling an alcoholic solution of potassium sulfide with excess ethyl iodide. It is apparent that these two methods are practically identical, the only difference being that in the latter the diethyl sulfide

$$K_2S + 2C_2H_5I \longrightarrow C_2H_5SC_2H_5 + 2KI$$

$$C_2H_5SC_2H_5 + C_2H_5I \longrightarrow (C_2H_5)_3SI$$

is made as used. He noted that the salt is colorless, odorless and soluble in water, from which it can be recrystallized. He observed that the odor of diethyl sulfide could be detected over

its warm aqueous solution. He found the salt to be soluble in alcohol and chloroform, and insoluble in ether.

In addition to the iodide, Oefele prepared the nitrate by treating the iodide with silver nitrate, and the hydroxide by shaking an aqueous solution of the iodide with silver oxide. He found the hydroxide to be strongly basic and to decompose rapidly when exposed to the air. From it he easily prepared the sulfate, the oxalate and the chloride by treating the aqueous solution with the appropriate acid. He noted that all these salts are strongly deliquescent. By treating the chloride with platinous chloride, he obtained the double salt, which could be precipitated by the addition of alcohol, was stable in air and otherwise suitable for analysis.

$$(C_2H_5)_3SCl + PtCl_2 \longrightarrow (C_2H_5)_3SPtCl_3$$

Oefele recognized that the sulfonium compounds represent a quadrivalent form of sulfur, which he believed could be oxidized to hexavalent sulfur, since, on treating triethyl sulfonium iodide with iodine, two atoms of iodine are added.

$$(C_2H_5)_3SI + I_2 \longrightarrow (C_2H_5)_3SI_3$$

Oefele's discovery immediately attracted attention, and his results were soon confirmed and amplified by other workers. Cahours (2) (3) (4) (5) (6) prepared the corresponding trimethyl sulfonium compounds and attempted an extensive investigation into the mechanism of the general reaction. In the course of this investigation he brought about the reaction of methyl sulfide with methyl chloride, bromide, and iodide,

respectively, to obtain the corresponding sulfonium derivatives. He prepared the corresponding ethyl, methyl and butyl compounds in an analogous manner. He also investigated the reactions of benzyl sulfide with methyl iodide and of benzyl bromide with methyl sulfide, as well as those which are represented by the following equations. These and the previously mentioned reactions were carried out at 100° in sealed tubes. The mechanism of these reactions, which Cahours believed is indicated by these equations, will be discussed later.

$$3C_2H_5SH + HI \longrightarrow (C_2H_5)_3SI + 2H_2S$$

$$3CH_3SH + HI \longrightarrow (CH_3)_3SI + 2H_2S$$

$$3(CH_3)_2S + C_2H_4Br_2 \longrightarrow 2(CH_3)_3SBr + C_2H_4S$$

$$2(CH_3)_2S + CH_3\overset{\overset{O}{\|}}{C}Br \longrightarrow (CH_3)_3SBr + CH_3\overset{\overset{O}{\|}}{C}SBr$$

$$2(CH_3)_2S + BrCN \longrightarrow (CH_3)_3SBr + CH_3SCN$$

$$CH_3SCN + 2CH_3I \longrightarrow (CH_3)_2SI + CNI$$

$$C_7H_7Br + (CH_3)_2S \xrightarrow{CH_3OH} (CH_3)_3SBr + C_7H_7OCH_3 + H_2O$$

$$C_7H_7Br + (CH_3)_2S + CH_3OH \longrightarrow (CH_3)_3SBr + C_7H_7OH$$

C. Sholler (7) was the first to investigate sulfonium compounds containing an aromatic group. He brought about the reaction between benzyl sulfide and methyl iodide. Contrary to his expectations, he did not obtain dibenzyl-methyl sulfonium iodide, but benzyl-dimethyl sulfonium iodide and trimethyl sulfonium iodide. The reaction was

carried out in sealed tubes at room temperature and at 100°. In the former case, the main product was benzyl-dimethyl sulfonium iodide; in the latter case, it was trimethyl sulfonium iodide. Both compounds were isolated in the form of their platinic chloride double salts. His explanation of these facts is represented by the following equations:

$$(C_7H_7)_2S + 2CH_3I \longrightarrow 2C_7H_7I + (CH_3)_2S$$

$$(CH_3)_2S + C_7H_7I \longrightarrow (CH_3)_2C_7H_7SI$$

$$CH_3I + (CH_3)_2S \longrightarrow (CH_3)_3SI$$

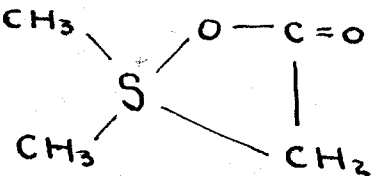
This mechanism will be discussed later also. Kruger (8) and Dehn (9) (10) obtained results similar to those of Oefele, Scholler and Cahours.

Most of the work that has been done since on aliphatic sulfonium compounds has been largely on the same types of reaction applied to the formation of compounds containing other alkyl groups or other anions. Crum-Brown and Blaikie (11) prepared trimethyl sulfonium sulfate, sulfite, sulfide, oxalate, and dithionate. Ferrer (12) formed xanthates by the action of triethyl sulfonium hydroxide and carbon disulfide.

Klinger (13) obtained trimethyl sulfonium iodide by treating pure sulfur with methyl iodide in a sealed tube at 160-190°. Renshaw, Bacon and Roblyer (14) obtained β-hydroxy-ethyl sulfonium compounds by treating methyl sulfide with β-iodo-ethyl alcohol. Ettel and Kohlik (15) obtained similar compounds. Bennett and Hock (16) (17) studied analogous reactions in which the alkyl hydroxyl group was replaced by a halogen atom.

Smiles (18) found that ω-halogen ketones react with alkyl sulfides

to form sulfonium salts, and Delisle)19) prepared dimethyl thetine by the action of bromacetic acid on dimethyl sulfide.

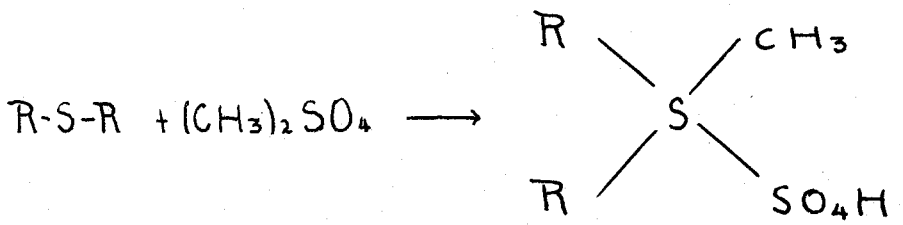


Monothio- and dithio-ethylene glycol and triethyl sulfonium hydroxide were prepared by Chichibabin (20) (21) by the action of hydrogen sulfide on ethylene oxide. Davies (22) found that trimethyl sulfonium iodide is formed by the action of methyl iodide on methyl poly-sulfides. Similar results were obtained by Steinkopf and Müller (23).

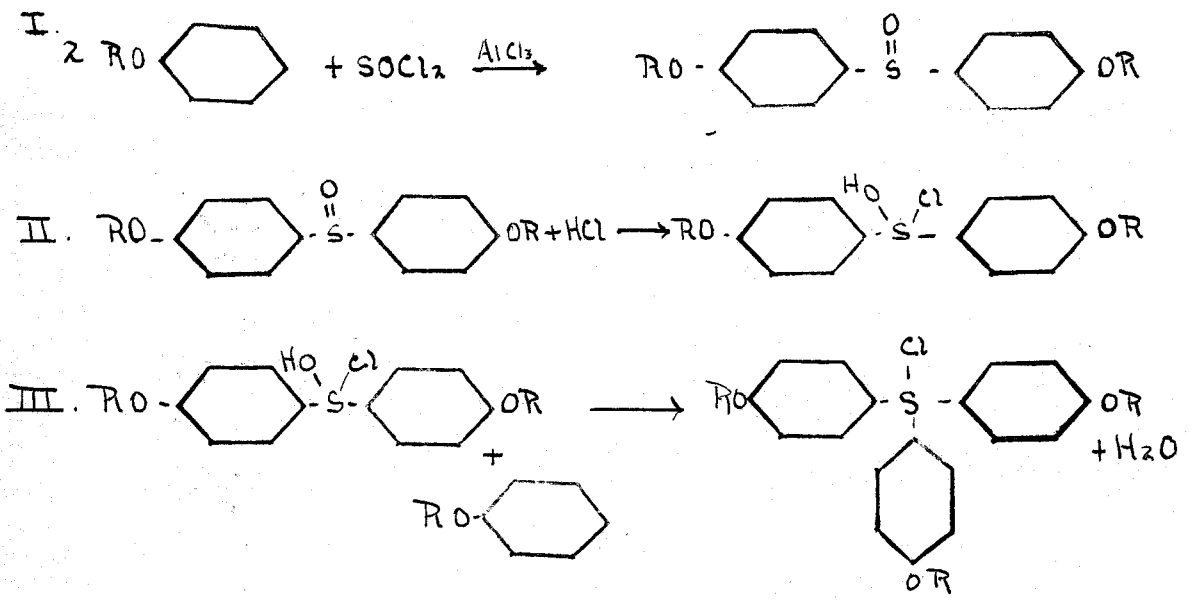
The difficulty in bringing about the reaction of an alkyl sulfide with an alkyl iodide has been found to increase with the increasing molecular weight of the reactants (24). This is especially true in the case of the molecular weight of the halide. Methyl iodide, for example, reacts with amyl sulfide much more readily than amyl iodide with methyl-amyl sulfide. Hughes and Ingold (25) found that, if nitro-methane is used as a solvent, the reaction takes place readily in both cases. Smiles (26) found that, by adding mercuric iodide to a mixture of an alkyl sulfide and an alkyl iodide at room temperature, the time for complete reaction was reduced from three days to 10-15 minutes. The sulfonium compound was obtained in the form of its mercuri-iodide double salt. Hilditch and Smiles (27) used this method to form dibenzyl-methyl sulfonium iodide, which neither Schöller nor Cahours had been able to obtain (pages 3,4).

The discussion, thus far, has dealt with only those sulfonium compounds in which the carbon atoms attached to the sulfur were aliphatic in character. All the early attempts to synthesize aromatic sulfonium compounds had failed, and the statement was made (28) (29) that aromatic sulfonium bases do not exist. However, several general methods of preparation are now known:

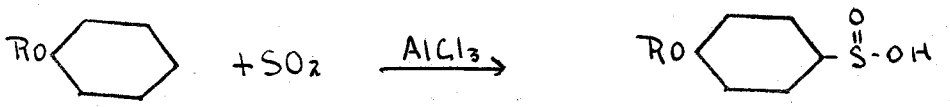
1. By the action of dimethyl sulfate on aromatic sulfides or thiophenols (30) (31);



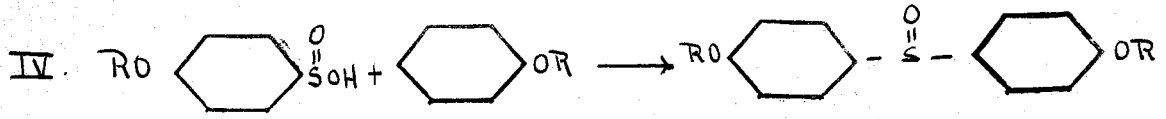
2. By the action of thionyl chloride on toluene, xylene, phenol, dimethyl aniline, etc., in the presence of aluminium chloride or other dehydrating agents (32) (33) (34) (35) (36) (37) (38) (39);



3. By the action of sulfur dioxide and aluminium chloride on aromatic compounds such as phenolic ethers (40). A sulfinic acid is formed first. This then reacts with another molecule of the phenolic ether to form a sulfoxide. The reaction then proceeds in conformity with the equations given in 2.



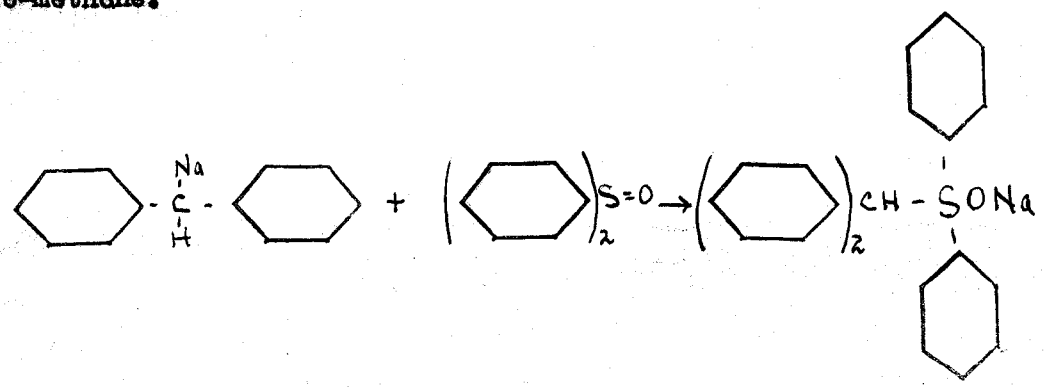
IV.



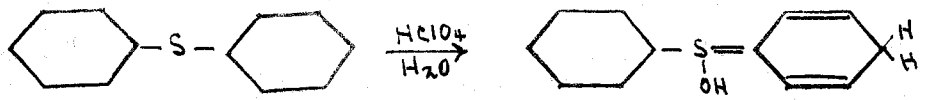
4. By the action of a sulfinic acid on an aromatic compound in the presence of a dehydrating agent such as H_2SO_4 or P_2O_5 ; Equation IV.

5. By the condensation of an aromatic sulfoxide with other aromatic compounds; Equations II and III.

Schonberg and Stephenson (41) obtained an aromatic sulfonium compound in an unusual way by treating diphenyl sulfoxide with diphenyl-sodio-methane.



Hinsberg (42) (43) reported an interesting reaction, which occurred on treatment of diphenyl sulfide with perchloric acid and water.



He obtained the perchlorate of the sulfonium salt in two forms, which, on heating, decomposed into diphenyl sulfide and an iso-diphenyl sulfide respectively. He attempted to explain the isomerism on the basis of two centers of valence for the sulfur atom.

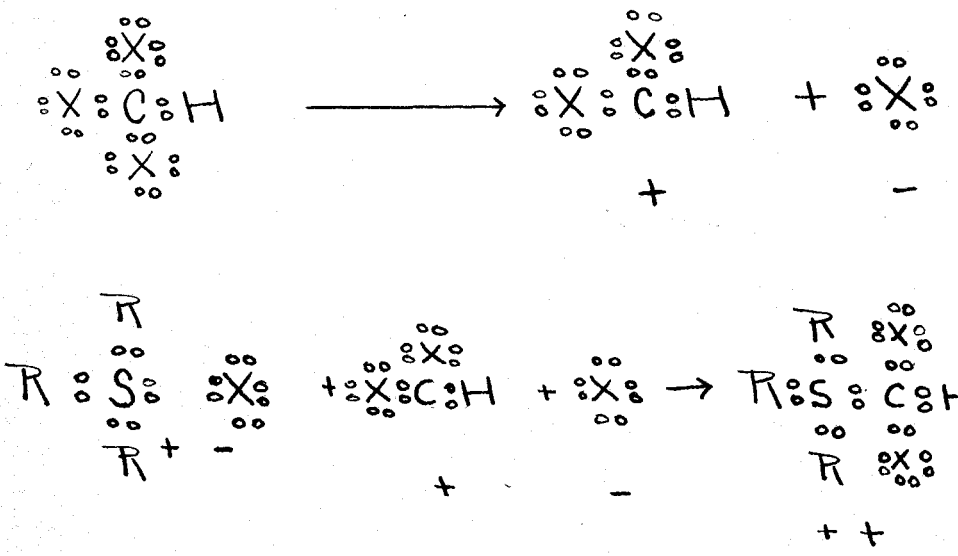
The existence of isomers of this nature seems very unlikely from stereochemical considerations. In addition, Hinsberg's analyses of these compounds are not accurate enough to be conclusive. Some of the compounds could not be obtained in a crystalline form, indicating that he may not have been working with pure substances. The so-called isomers may easily have been compounds of nearly the same percentage composition, which had been formed by the vigorous treatment, such as reaction with perchloric acid and high temperature distillation, to which the reaction mixture had been subjected.

It was noted previously that, in many instances, sulfonium compounds have been isolated in the form of their double salts with platinum or mercury. These compounds have themselves attracted a considerable amount of interest and have been thoroughly studied (44). In addition to those with platinum and mercury, the double salts with gold chloride, silver cyanide, and zinc, cadmium, silver, antimony, bismuth, tin, manganese, iron and copper halides have been studied (8) (45) (46) (47) (48) (49) (50).

Similar complexes with chloroform, bromoform and iodoform have also been studied (51) (52) (53) (54), and Dobbin and Masson (55) prepared

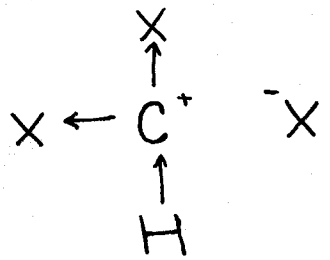
sulfonium chloro-, bromo-, and iodo-chlorides, bromides and iodides.

In the case of the latter compounds, it seems probable that the haloform molecule loses a halogen ion with a complete octet of electrons. The CHX_2^+ group then coordinates with the unshared pair of electrons belonging to the sulfonium atom. This neutralizes the carbon atom, but increases the positive charge of the sulfur atom from one to two, due to the sharing of its previously free electrons.

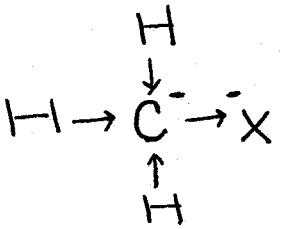


The sulfur, therefore, has four covalences and two polar valences as in the case of sulfuric acid.

It will be noted that the ionization of the halogen atom takes place more readily in the haloform compound than in the methyl halides because of the fact that, in the former case (I), the two remaining halogen atoms cause an electron shift away from the carbon atom, making it more positive; in the latter case (II), the electron shift is away from the three hydrogen atoms, toward the carbon atom, making it more negative.



I



II

In I, the bond between the positive carbon and the negative halogen tends to become polar in character, whereas there is no such tendency in II. It is probably for this reason that sulfonium salts do not form complexes with, for example, methyl iodide.

II

STEREOISOMERISM OF SULFONIUM COMPOUNDS

Soon after the discovery of sulfonium compounds, the problem of the nature of the four valence bonds of the sulfur atom attracted attention. In 1876, Kruger (8) claimed that the reaction of methyl sulfide on ethyl iodide, and of methyl-ethyl sulfide on methyl iodide, produced different compounds.

$$(CH_3)_2S + C_2H_5I \longrightarrow (CH_3)_2SC_2H_5I$$

$$(CH_3)(C_2H_5)S + CH_3I \longrightarrow (CH_3)_2(C_2H_5)SCH_3I$$

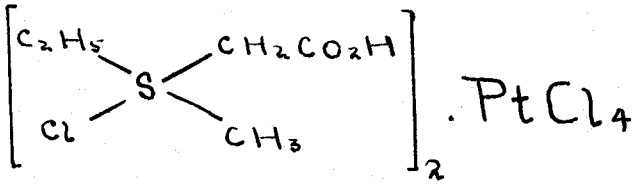
His work was apparently confirmed by Nasini and Scala (56) and, for a time, it was accepted that the three non-ionizing valences of the sulfur atom are not equivalent. However, Klinger and Maassen (57) (58) repeated this work, obtained identical products, and pointed out the source of error of the previous workers (which we discuss on page 26). Subsequent research has upheld the view that the three covalences are equivalent (59).

Many attempts were made to bring this view to its logical conclusion by obtaining an optically active sulfonium compound, the activity of which is due to the asymmetry of a central sulfur atom, whose four valence bonds, occupied by four different univalent groups, are non-planar. The isolation of a compound of this nature would also prove conclusively that the sulfonium compounds are atomic compounds rather than merely molecular addition products of an organic sulfide with a halide or sulfate.

Due to the instability and apparent ready racemization of these compounds, the results were, at first, all negative or ambiguous. Stromholm (60) had prepared a whole series of unsymmetrical sulfonium compounds

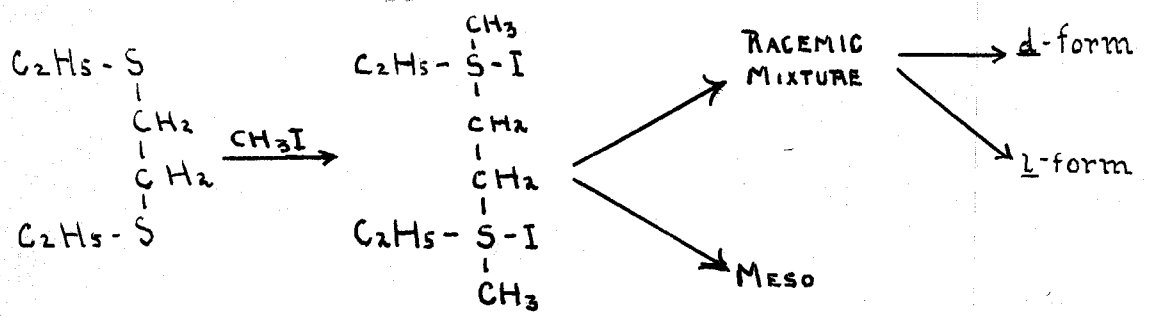
in an attempt to obtain one showing the requisite stereoisomerism. He examined the sulfonium salts of all of the following: methyl-ethyl-isopropyl; methyl-ethyl-n-propyl; methyl-ethyl-n-butyl; methyl-ethyl-isobutyl; methyl-ethyl-secondary butyl; methyl-ethyl-hexyl; methyl-dinormal-propyl; methyl-di-isobutyl; methyl-isopropyl-isobutyl; methyl-diamyl; methyl-ethyl-benzyl; methyl-isopropyl-benzyl; dimethyl-acetal; methyl-ethyl-acetal; methyl-isopropyl-thetine; methyl-isobutyl-thetine. In no case did he obtain evidence of stereoisomerism, and he concluded that the supposedly quadrivalent sulfur atom can not be similar to carbon as had been suspected. Pope and Peachey (62) prepared methyl-ethyl-thetine-d-camphorsulfonic acid but could not resolve it. They concluded that the four radicals lie in the same plane as the sulfur atom.

Later in 1900, however, Pope and Peachey (61) succeeded in preparing methyl-ethyl-thetine platinichloride and in isolating the d and l isomers, which owe their rotatory power to the presence of an asymmetric quadrivalent sulfur atom, and they thus proved that "in compounds of the type SX_4,



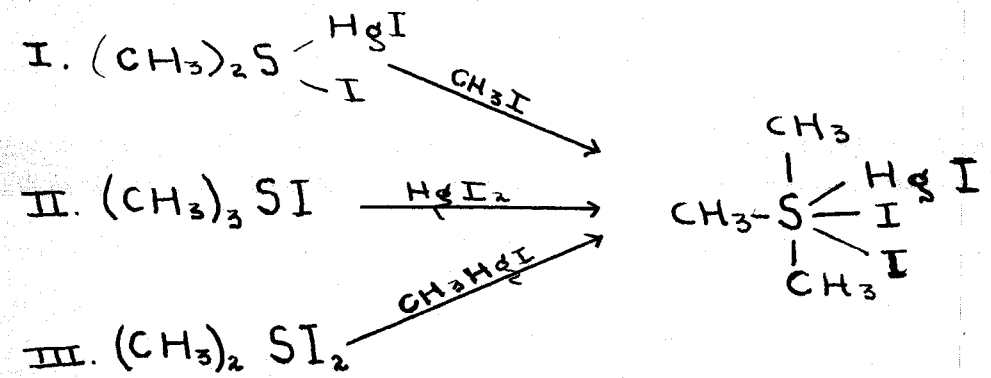
the sulfur atom is truly quadrivalent, and the four groups attached to it are, as in the case of carbon, situated at the apices of a tetrahedron, the interior of which is occupied by the sulfur atom". Similar results were obtained by Smiles (63) (64) (18) (65).

The stereochemistry of quadrivalent sulfur was extended to compounds having two asymmetric sulfur atoms by Wedekind (66), who isolated a meso compound and a racemic mixture from the reaction of methyl iodide and ethylene diethyl-dithio-ether.



The racemic mixture was separated into two optically active forms with d-camphorsulfonic acid.

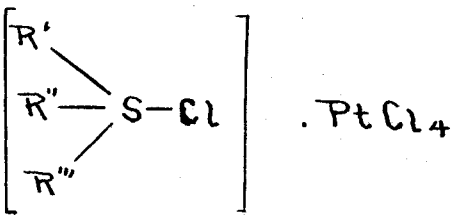
Many of the sulfonium compounds have been isolated in the form of their metal halide and haloform double salts. This complicating factor made it important, especially in view of the stereochemical considerations, that the valence of the sulfur atom in these double salts be definitely determined. Hilditch and Smiles (27) (67) held the view that the sulfur in these compounds is hexavalent, because such a representation gives rise to the simplest structure, and because sulfur is commonly hexavalent. Smiles (26) presented a considerable amount of chemical evidence in favor of this view. He pointed out that trimethyl-sulfonium-mercuri-iodide can be made in the three following ways:



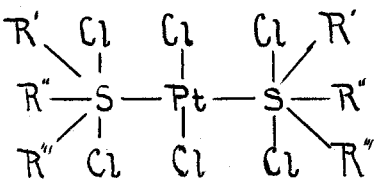
It will be noted, however, that he assumes that the sulfur in I and III is also quadrivalent. He also observed that if the addition products of halogens to sulfonium halides are not so-called molecular compounds, they

must contain hexavalent sulfur or tervalent iodine, probably the former, since sulfonium sulfates give similar compounds. One might point out that Smiles overlooked the fact that reactions II and III would give different molecular compounds but the same hexavalent compound.

If this view were correct, the stereoisomerism in compounds of the type



could not be explained by any of the accepted theories of stereochemistry since a structure similar to the one following, in which neither the sulfur nor the platinum is asymmetric, would have to be assigned to the compound.



This view fails to differentiate between polar and co-valences.

Cavel and Sugden (68) presented both chemical and physical evidence that the sulfur atom is quadrivalent in these compounds. They observed that a sulfonium iodide-mercuric iodide double salt will dissolve silver iodide. This can be explained by assuming that ionization takes place as follows;

$$R_3SI.HgI_2 \longrightarrow R_3S^+ + HgI_3^-$$

and that the HgI_3^- ion reacts with the iodide ion furnished by the silver iodide,

$$HgI_3^- + I^- \longrightarrow HgI_4^{--}$$

forming the more stable HgI_4^{--} ion.

Their measurements of the parachor also indicate that the structure of these complexes is

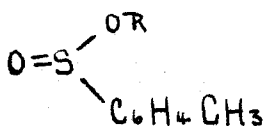
I $(R_3S)^+ HgI_3^-$

and not II $(R_3SHgI_2)^+ I^-$

Ray and Adhikary (69) arrived at the same conclusion after studying the conductivity of salts of this type. Furthermore, a consideration of the electronic arrangement, to be discussed later, shows such a hexavalent structure to be impossible.

Thus far we have omitted an important class of compounds, which, although not generally considered to be of the sulfonium type, have a quadrivalent sulfur atom and exhibit properties which make them important in any discussion of this nature. These compounds are the sulfoxides and sulfinic esters, $R-\overset{O}{\overset{\|}{S}}-R$ and $R-\overset{O}{\overset{\|}{S}}-O-R$.

Their classical structural formulae do not indicate that there would be any possibility of stereoisomerism. Yet Kenyon, et al, (70) (71) resolved the sulfinic esters,



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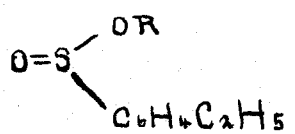
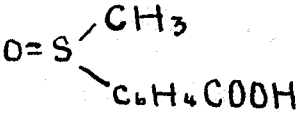
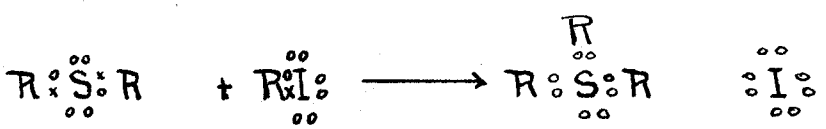


and the sulfoxide,



For an explanation of these facts, the structures of these compounds must be examined in the light of Lewis's electronic theory of valence as developed by Langmuir (72).

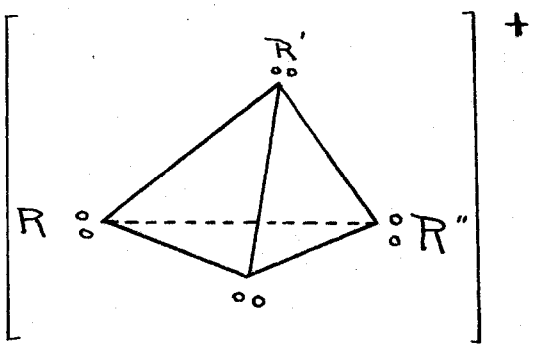
In the formation of the ordinary type of sulfonium compound, previously discussed, the sulfide, I., has two pairs of



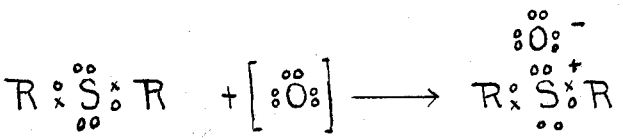
I II + -

unshared electrons. The alkyl radical of the organic halide, II, coordinates with one of these pairs. The sulfur atom, which in the sulfide had been neutral, thus acquires a positive charge due to the sharing of two of its previously free electrons. The iodine atom, on the other hand, acquires a negative charge because the two electrons, which had previously been shared with the carbon of the alkyl radical, are now free. It still has an outer shell of eight electrons and is, therefore, in a stable condition, as is the sulfur complex. In this type of sulfonium compound, therefore, the sulfur atom has a covalency of three holding the three univalent alkyl radicals, and a polar valency of one, by means of which the iodine atom is bound.

In the case where R, R' and R" are different, Pope and Peachey (61) and Smiles (64) found that the optical activity is not destroyed when the compound is in solution and ionized. This fact indicates conclusively that the groups R, R' and R", occupying three corners of the tetra-hedral sulfur atom, retain their relative positions even though the fourth corner is occupied only by electrons. In other words, a pair of electrons can contribute just as much as an atom or radical to the asymmetry of the central sulfur atom.

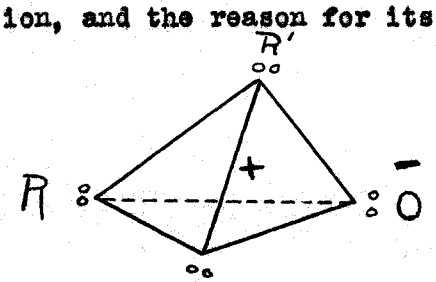


Extending this reasoning to the sulfoxides and sulfinates, the cause of their stereoisomerism immediately becomes apparent. When a dialkyl sulfide is oxidized, the neutral oxygen atoms, having only six electrons in its outer shell, coordinates with one of the free pairs of electrons of

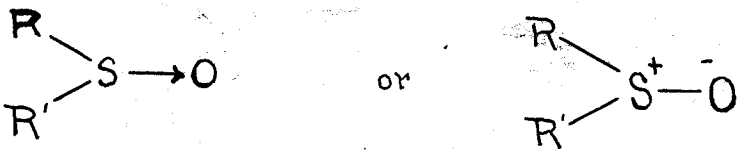


the sulfur atom. The octet of the oxygen atom is thus completed, but it now has an excess of one electronic charge above that necessary to neutralize its nuclear charge. Therefore, it is negatively charged. The previously neutral sulfur atom, on the other hand, has lost the equivalent of one electron necessary to completely balance its nuclear charge, and is, therefore, positively charged.

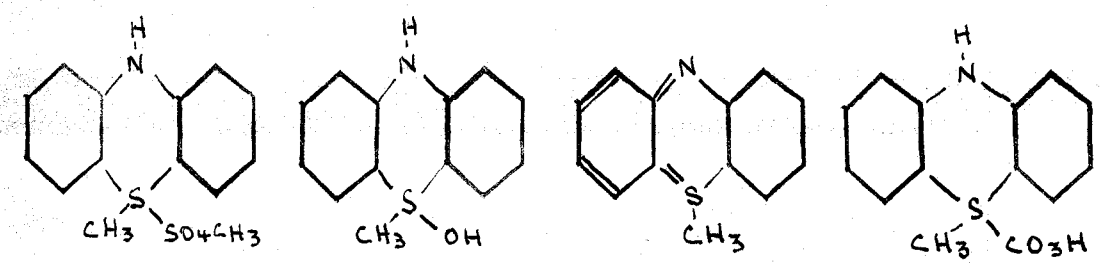
Thus, it is evident that, when R and R' are different, the same arrangement exists as in the case of the previously discussed optically active sulfonium ion, and the reason for its activity is explained.

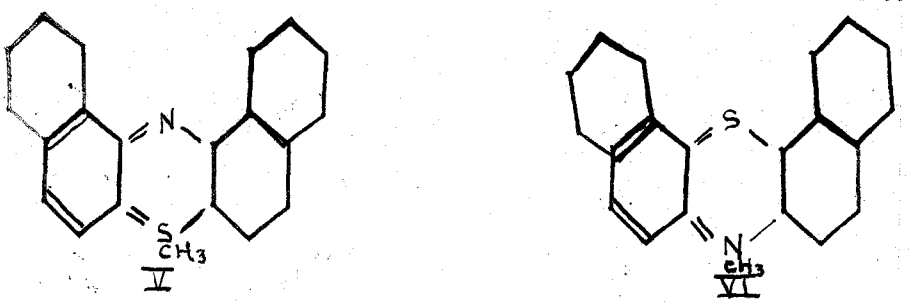


It will be noted, however, that in the case of the sulfoxides and sulfinic esters, the oxygen is bound to the sulfur atom by <u>both</u> a covalence and a polar valence. This is known as a semi-polar double bond. It is represented by either an arrow showing the direction of transfer of an electronic charge or by plus and minus signs:



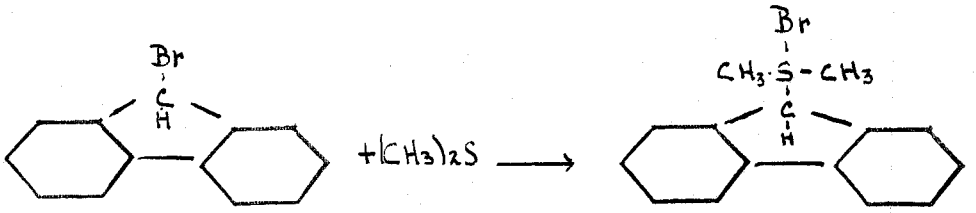
Kehrmann, et al, (73) (74) reported a series of compounds which apparently contain a semi-polar double bond between carbon and sulfur. However, they used the classical system of notation and apparently did not recognise the possibility of this fact. They obtained the first of this series by treating thiodiphenylamine with methyl sulfate, and obtained I., which, by means of alkali, they transformed into the colorless base, II. This was easily dehydrated, yielding III, an intensely yellow, unstable substance which can be transformed with carbon dioxide into the colorless carbonate, IV. The corresponding naphthalene derivatives behave in an analogous manner, V and VI.



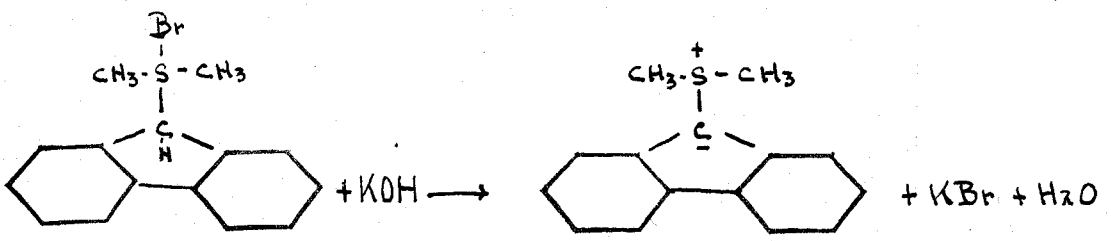


It will be noted that the presence of a nitrogen atom is a complicating factor, since there may be a bond between it and the sulfur atom. However, the intense color of III and IV indicates that a quinoid structure, as represented, is very likely.

Ingold and Jessop (75) have also reported the case of a semi-polar double bond between carbon and sulfur. They treated 9-bromofluorene with methyl sulfide in nitromethane solution, and obtained 9-fluorene-dimethyl-sulfonium bromide.



Upon treating this compound with dilute alkali, they obtained dimethyl-sulfonium-9-fluorenylidide, which precipitated from the aqueous solution

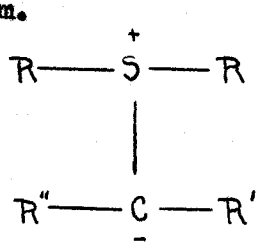


as bright yellow leaflets. These were very unstable, however, and could not be kept, even in a vacuum, for more than a few hours. The authors were able to obtain an analysis, however, which corresponded with the proposed formula. The molecular weight was determined cryoscopically in benzene by plotting the changing apparent molecular weight of the decomposing substance against time, and extrapolating to zero time. This determination also checked with the proposed formula, indicating that the authors had probably been

successful in obtaining a compound containing a semi-polar double bond between carbon and sulfur. We attempted to repeat this work but found that the semi-polar compound decomposed before we could remove it from the reaction vessel.

Hughes and Kuriyan (76) continued this work. Instead of using fluorene itself as a starting point, they used 2-nitrofluorene and 2-7-dinitrofluorene, and then went through the same series of reactions that Ingold and Jessop had attempted. They found that the semi-polar compound made from mono-nitrofluorene showed an increase in stability, though still unstable, and that the compound prepared from dinitrofluorene was relatively stable. They obtained the latter in the form of red, dichromate-like crystals, suitable for analysis. They were able to reconvert it to its several sulfonium salts.

Although this chemical evidence indicated that a compound containing a semi-polar double bond between carbon and sulfur has been prepared, it is desirable, in order to prove this beyond a doubt, to obtain an optically active compound in which the activity would be due to a carbon atom, having two of its valence bonds occupied by different univalent radicals, the third by the sulfur covalence and the fourth by the polar valence with the quadrivalent sulfur atom.



The resolution of such a compound would definitely prove the existence of a semi-polar double bond between carbon and sulfur. This was the object of our research.

III

MECHANISM FOR THE DECOMPOSITION OF SULFONIUM SALTS

In the present work 2-fluorene-phenyl-bromomethane was selected as the starting substance because it has the required asymmetry and because its bromine atom was thought to be very active. In addition, since 2-fluorene-phenyl nitromethane is more stable than 9-nitrofluorene, (77) it was hoped that the corresponding sulfonium derivative might also show the same increase in stability.

Due to the success which Ingold and Jessop (75) had with the use of nitromethane as a solvent in preparing sulfonium compounds, their method was tried first. 2-fluorene-phenyl-bromomethane was dissolved in nitromethane and treated with an excess of methyl sulfide. At room temperature little or no reaction took place even on standing several days. The same reaction was therefore tried at higher temperatures using a sealed tube to prevent loss of the highly volatile dimethyl sulfide. Two runs were made at 100° C., and in each case trimethyl-sulfonium bromide was one of the products. Three other products were obtained in the first run and one (V) in the second. Of these, only one contained sulfur, as will be noted in Table I.

In view of the number of compounds obtained and the inconsistency of the results, it seemed probable that the nitromethane had entered the reaction in some way, probably as a methylating agent since none of the compounds were found to contain nitrogen.

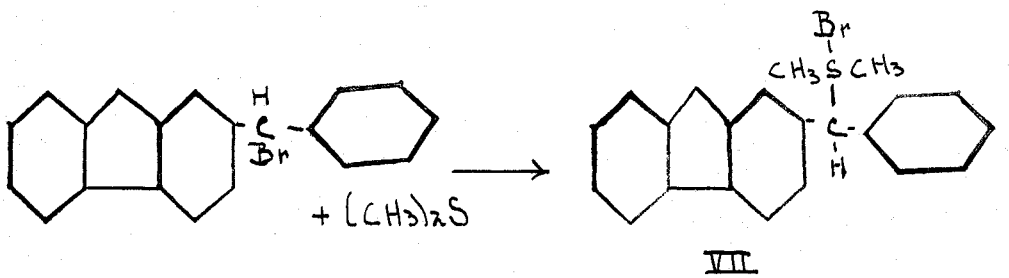
In an attempt to explain the formation of the trimethyl-sulfonium bromide, it was assumed that the desired sulfonium compound, VII, had been formed and had immediately decomposed into VI and methyl bromide. The methyl bromide must then have reacted with the excess dimethyl

sulfide, forming trimethyl-sulfonium bromide.

Table I.

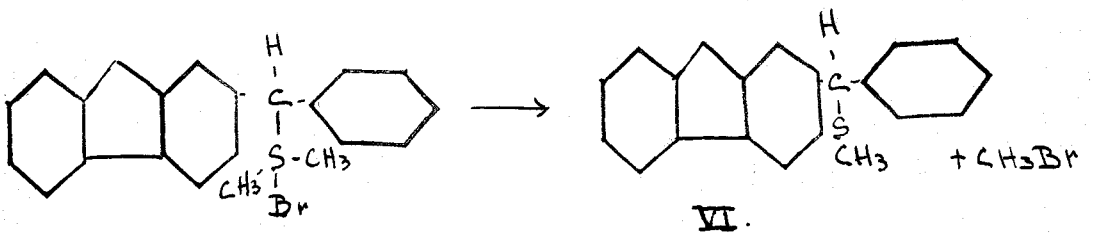
Cpd. #	m.p.° C	Sulfur	Halogen	Nitrogen	Identified
I.	225-35	None	None	None	
II.	178	Positive	Positive	None	$(CH_3)_2SBr$
III.	248-50	None	24.02%	None	
IV.	88-90	None	None	None	
V.	105	None	None	None	

A.



VII

B.



VI.

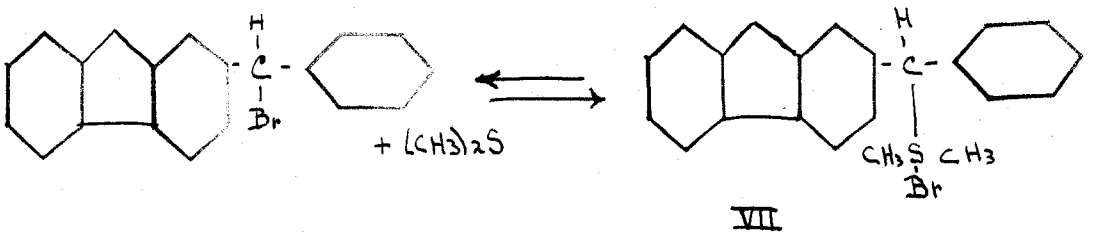
C. $(CH_3)_2S + CH_3Br \longrightarrow (CH_3)_3SBr$

If this were the case, VI must have reacted further with nitromethane to give I, III, IV, and V.

It was considered advisable, therefore, to try the same reaction in the absence of nitromethane. The reaction was run in a sealed tube at 100° C as before, and two compounds were isolated. One was trimethyl-sulfonium bromide, and the other was a compound melting at 109.5° C. This was proved by analysis to be the sulfide, VI, as predicted by the proposed mechanism.

Since, according to this new mechanism, the sulfonium compound must

have another molecule of dimethyl sulfide with which to react in order to form trimethyl-sulfonium bromide, this suggested a method of testing the feasability of the mechanism. A run was made using 2-fluorene-phenyl-bromomethane and dimethylsulfide in equimolar quantities. A sealed tube at 100° C. was employed as before. Contrary to our expectations, the same two compounds were obtained as when the dimethyl sulfide was used in excess, and exactly one half of the starting quantity of the bromide was isolated unchanged. It is very likely, therefore, that there is an equilibruim set up between the sulfonium compound on the one hand, and the bromide-sulfide mixture on the other, in which there is always enough

A. 

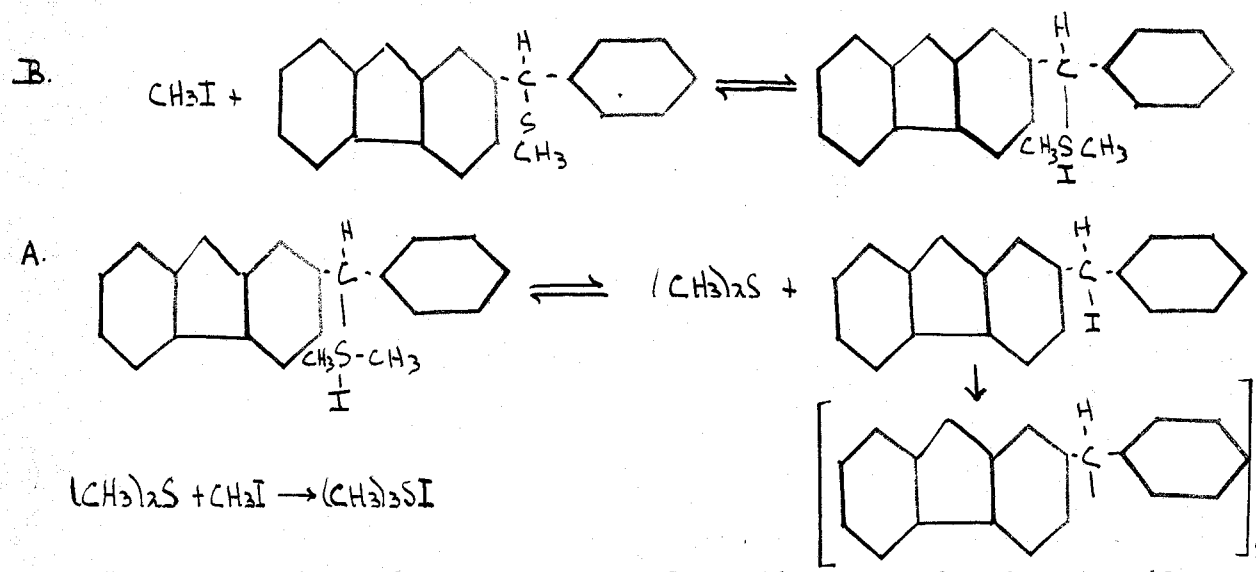
VII

sulfide present to react with the methyl bromide formed when VII decomposes as shown in equation B. The final results indicate that; (1) reaction A is certainly reversible; (2) there is probably very little of the complex sulfonium compound, VII, present at any time.

In order to test this mechanism further, and to determine whether or not reaction B is reversible, the (2-fluorene-phenyl-methyl)-methyl sulfide VI, was treated with methyl iodide at room temperature and at 100° C. in sealed tubes. In both cases trimethyl-sulfonium iodide was one of the products formed, but the anticipated 2-fluorene-phenyl-iodomethane, IX, could not be isolated. Instead, an hydrocarbon melting at 165° C. was

found. The failure to isolate the expected iodide was not surprising since previous attempts to make it by ordinary methods had failed due to its instability. 2-fluorene-phenyl-bromomethane is very active, and the corresponding iodo-compound should show an even greater activity.

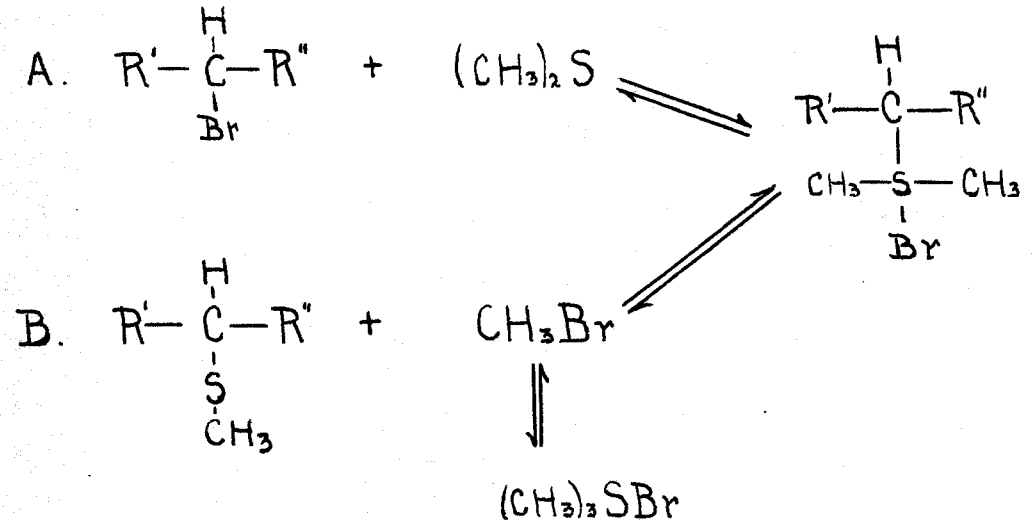
Due to the fact, that a considerable quantity of iodine was found in the reaction mixture, it seemed probable that sym-di-2-fluorene-diphenyl ethane, VIII had been formed with the liberation of iodine. To test this possibility an ethereal solution of 2-fluorene-phenyl-bromomethane was treated with sodium in the Wurtz-Fittig reaction. A compound was isolated from the reaction mixture which proved to be identical with VIII according to its melting point and mixed melting point.



In order to investigate the proposed reaction mechanism further, (2-fluorene-phenyl-methyl)-methyl sulfide was treated with excess ethyl iodide in a sealed tube at 100° C. Methyl-diethyl-sulfonium iodide again was isolated from the reaction mixture, but no other product could be obtained pure due to the large quantity of iodine present.

It is apparent, from this series of reactions, that reaction B as well as reaction A must be reversible. The complex sulfonium salt, therefore, is probably formed in small quantities. Regardless of the direction

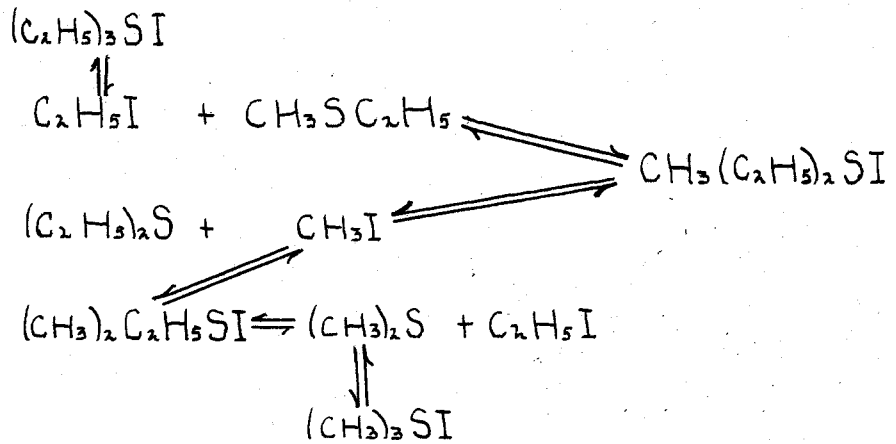
from which it is approached, it immediately decomposes in two directions, and the final products are those which are most stable at the temperature employed. A diagram of the whole mechanism may be represented as follows, with the reaction starting at either A or B.



The decomposition products of sulfonium compounds had been noted at an early date. Klinger and Maassen (58), in their proof of the equivalency of the valence bonds of the sulfur atom, had noted that methyl-ethyl sulfide could react with ethyl iodide to give methyl iodide and ethyl sulfide.

$$C_2H_5I + CH_3SC_2H_5 \longrightarrow CH_3I + (C_2H_5)_2S$$

In the light of our proposed mechanism, this apparently improbable reaction is easily explained by the intermediate formation of methyl-diethyl sulfide and its subsequent decomposition into methyl iodide and diethyl sulfide.



It will be noted that the methyl iodide can then react with the methyl-ethyl sulfide, forming dimethyl-ethyl-sulfonium iodide, which, in turn, can decompose into dimethyl sulfide and ethyl iodide. The dimethyl sulfide can then react with the methyl iodide to form trimethyl-sulfonium iodide. In addition, ethyl iodide can react with diethyl sulfide to give triethyl-sulfonium iodide. In this way, four different sulfonium compounds can be formed from the two simple starting substances. This undoubtedly accounts for much of the early confusion as to the nature of the sulfonium salts (8) (56).

Scholler (7), as previously mentioned (page 3), studied the reaction of benzyl sulfide with methyl iodide and proposed the most widely accepted mechanism for the formation of the decomposition products of a complex sulfonium salts. From the reaction of methyl iodide with benzyl sulfide at room temperature and at 100° , He obtained ,in each case, tri-

methyl-sulfonium iodide, dimethyl-benzyl sulfonium iodide and benzyl iodide. The mechanism which he proposed for the reaction is as follows:

$$4\ CH_3I + 2\ (C_7H_7)_2S \longrightarrow 4\ C_7H_7I + 2\ (CH_3)_2S$$

$$(CH_3)_2S + C_7H_7I \longrightarrow C_7H_7(CH_3)_2SI$$

$$(CH_3)_2S + CH_3I \longrightarrow (CH_3)_3SI$$

add: $$5\ CH_3I + 2\ (C_7H_7)_2S \longrightarrow 3\ C_7H_7I + C_7H_7(CH_3)_2SI + (CH_3)_3SI$$

It is very unlikely that there would be a direct interchange of sulfur and iodine between the benzyl sulfide and the methyl iodide as he proposes. It seems much more probable, because of this, and because of the thermal instability of the higher sulfonium compounds, which is demonstrated by the fact that the dimethyl-benzyl-sulfonium iodide was formed in much larger quantities at room temperature than at 100°, that the methyl-dibenzyl-sulfonium iodide was formed first and then immediately decomposed as shown, in conformity with the new mechanism which we have proposed.

$$2\ CH_3I + 2\ (C_7H_7)_2S \longrightarrow 2\ (C_7H_7)_2CH_3SI$$

$$2\ (C_7H_7)_2CH_3SI \longrightarrow 2\ C_7H_7SCH_3 + 2\ C_7H_7I$$

$$2\ C_7H_7SCH_3 + 2\ CH_3I \longrightarrow 2\ (CH_3)_2C_7H_7SI$$

$$(CH_3)_2C_7H_7SI \longrightarrow C_7H_7I + (CH_3)_2S$$

$$(CH_3)_2S + CH_3I \longrightarrow (CH_3)_3SI$$

add: $$5\ CH_3I + 2\ (C_7H_7)_2S \longrightarrow 3\ C_7H_7I + C_7H_7(CH_3)_2SI + (CH_3)_3SI$$

According to the concept of the reversibility of these reactions which we have introduced, the final products would have been the same if Scholler had started with the proper quantities of benzyl iodide and dimethyl sulfide. The equilibrium is always displaced in the direction which favors the formation of the most stable compounds. In the case of the sulfonium compounds (78), the most stable are the ones having the smallest groups.

Cahours' (2) (3) (4) (5) (6) studies of the reactions of many organic iodides with sulfides led him to propose a reaction mechanism, which is largely a series of chemical equations showing the reactants and the products. He represents the reaction of benzyl sulfide with methyl iodide as follows:

$$(C_7H_7)_2S + 3\ CH_3I \longrightarrow (CH_3)_3SI + 2\ C_7H_7I$$

He evidently failed to isolate the dimethyl-benzyl-sulfonium iodide which Schöller had noted. He probably allowed the reaction to proceed for too long a time at the temperature employed, 100°, thus favoring the decomposition of the higher sulfonium salt and the formation of trimethyl-sulfonium iodide. Our mechanism for this reaction has already been discussed.

Cahours also studied the reaction of benzyl bromide on dimethyl sulfide, which he represented as follows:

$$C_7H_7Br + 2\ (CH_3)_2S \longrightarrow (CH_3)_3SBr + C_7H_7SCH_3$$

This reaction can be explained by the new mechanism as indicated below:

$$C_7H_7Br + 2\ (CH_3)_2S \rightleftharpoons CH_3-\underset{\displaystyle Br}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{S}}}}-C_7H_7$$

$$C_7H_7SCH_3 + CH_3Br \rightleftharpoons CH_3-\underset{\displaystyle Br}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{S}}}}-C_7H_7$$

$$CH_3Br \rightleftharpoons (CH_3)_3SBr$$

The failure of the benzyl bromide to react further with the methyl-benzyl sulfide is undoubtedly due to the fact that it reacts preferentially with the simpler alkyl sulfide.

We believe that all of the following reactions which Cahours studied can be explained more simply and logically by our mechanism. His representation, A, is followed immediately in each case by ours, B.

A. $3\,C_2H_5SH + HI \rightarrow (C_2H_5)_3SI + 2\,H_2S$

B. $2\,C_2H_5SH + 2HI \rightarrow 2\,C_2H_5\overset{H}{\underset{I}{\dot{S}}}H \rightarrow 2\,C_2H_5I + 2\,H_2S$

$C_2H_5SH + C_2H_5I \rightarrow (C_2H_5)_2S\overset{H}{\underset{I}{\dot{}}} \rightarrow (C_2H_5)_2S + HI$

$(C_2H_5)_2S + C_2H_5I \rightarrow (C_2H_5)_3SI$

---

add: $3\,C_2H_5SH + 2HI \rightarrow (C_2H_5)_3SI + 2\,H_2S$

A. $3(CH_3)_2S + C_2H_2Br_2 \rightarrow 2(CH_3)_3SBr + C_2H_2S$

B. $(CH_3)_2S + BrCH=CHBr \rightarrow CH_3\overset{CH_3}{\underset{Br}{\dot{S}}}CH=CHBr$

$CH_3\overset{CH_3}{\dot{S}}CH=CH\text{-}Br \rightarrow CH_3SCH=CHBr + CH_3Br$

$CH_3SCH=CHBr \rightarrow CH_3\text{-}S\text{-}CH$ (Br, $\overset{\|}{C}H$)

$CH_3\text{-}S\text{-}CH$ (Br, $\overset{\|}{C}H$) $\rightarrow CH\equiv CH + CH_3Br$

$2\,CH_3Br + (CH_3)_2S \rightarrow 2(CH_3)_3SBr$

---

add: $3(CH_3)_2S + C_2H_2Br_2 \rightarrow 2(CH_3)_3SBr + C_2H_2S$

A. $2(CH_3)_2S + CH_3\overset{O}{\overset{\|}{C}}Br \longrightarrow (CH_3)_3SBr + CH_3\overset{O}{\overset{\|}{C}}SCH_3$

B. $(CH_3)_2S + CH_3\overset{O}{\overset{\|}{C}}Br \longrightarrow CH_3-\underset{Br}{\overset{CH_3}{\underset{|}{\overset{|}{S}}}}-\overset{O}{\overset{\|}{C}}-CH_3$

$CH_3\underset{Br}{\overset{CH_3}{\underset{|}{\overset{|}{S}}}}-\overset{O}{\overset{\|}{C}}-CH_2 \longrightarrow CH_3Br + CH_3S\overset{O}{\overset{\|}{C}}-CH_3$

$CH_3Br + (CH_3)_2S \longrightarrow (CH_3)_3SBr$

add: $2(CH_3)_2S + CH_3-\overset{O}{\overset{\|}{C}}-Br \longrightarrow (CH_3)_3SBr + CH_3S\overset{O}{\overset{\|}{C}}-CH_3$

A. $2(CH_3)_2S + BrCN \longrightarrow (CH_3)_3SBr + CH_3SCN$

B. $(CH_3)_2S + BrCN \longrightarrow CH_3\underset{Br}{\overset{CN}{S}}CH_3$

$CH_3\underset{Br}{\overset{CN}{S}}CH_3 \longrightarrow CH_3Br + CH_3SCN$

$CH_3Br + (CH_3)_2S \longrightarrow (CH_3)_3SBr$

add: $2(CH_3)_2S + BrCN \longrightarrow (CH_3)_3SBr + CH_3SCN$

A. $CH_3SCN + 2CH_3I \longrightarrow (CH_3)_3SI + CNI$

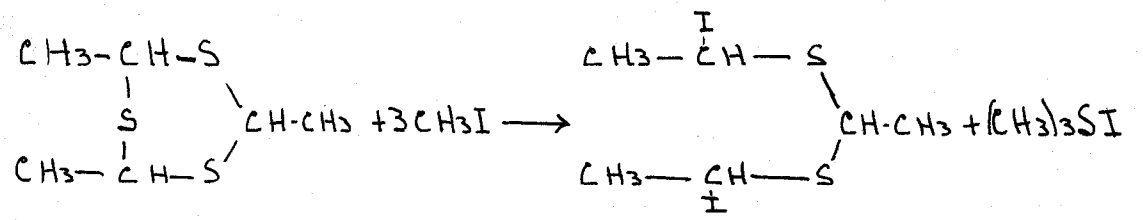
B. $CH_3SCN + CH_3I \longrightarrow CH_3\underset{I}{\overset{CH_3}{S}}CN$

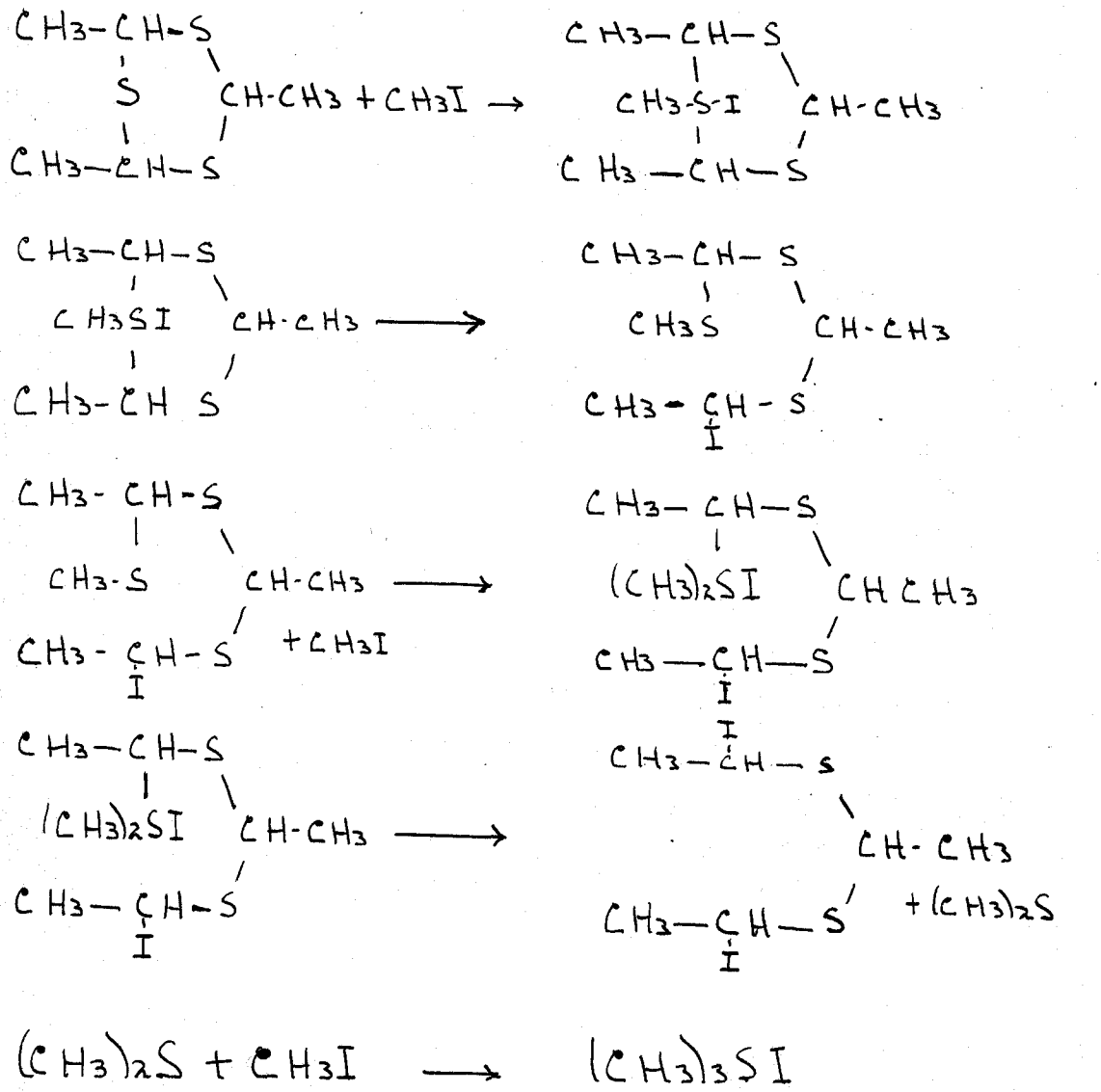
$(CH_3)_2S\underset{I}{-CN} \longrightarrow CH_3SCH_3 + CNI$

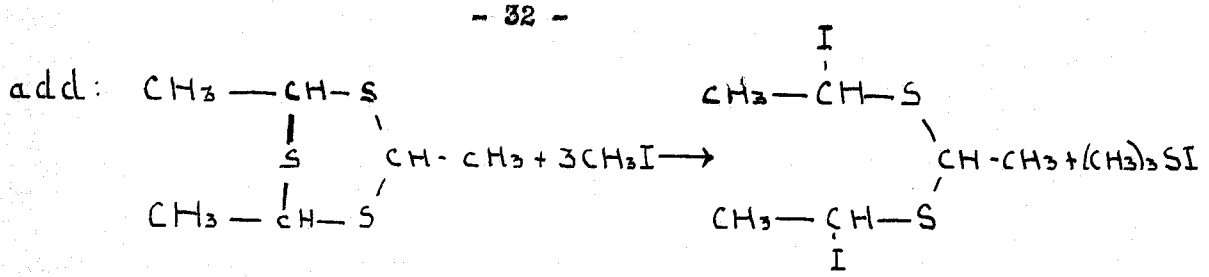
$CH_3SCH_3 + CH_3I \longrightarrow (CH_3)_3SI$

add: $CH_3SCN + 2CH_3I \longrightarrow (CH_3)_3SI + CNI$

Klinger (13), while working with trithioacetaldehyde, noted the following reaction, which is also easily explained on the basis of our theory:

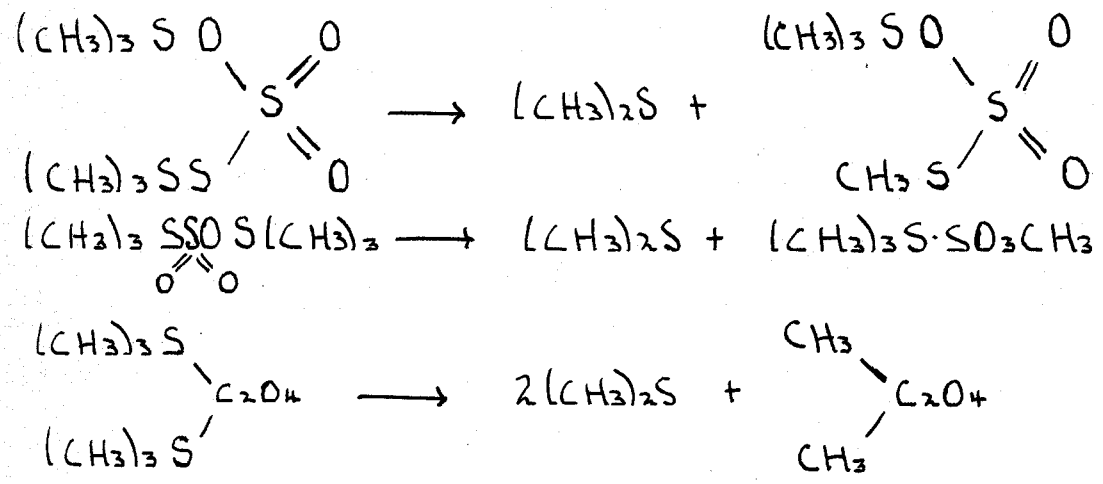
A. 

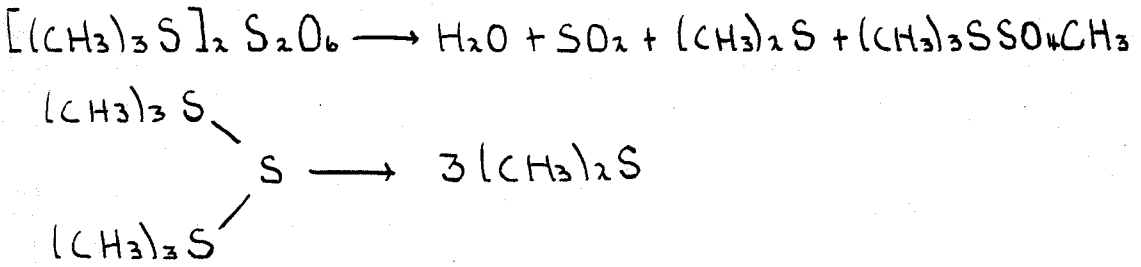
B. 

add: 

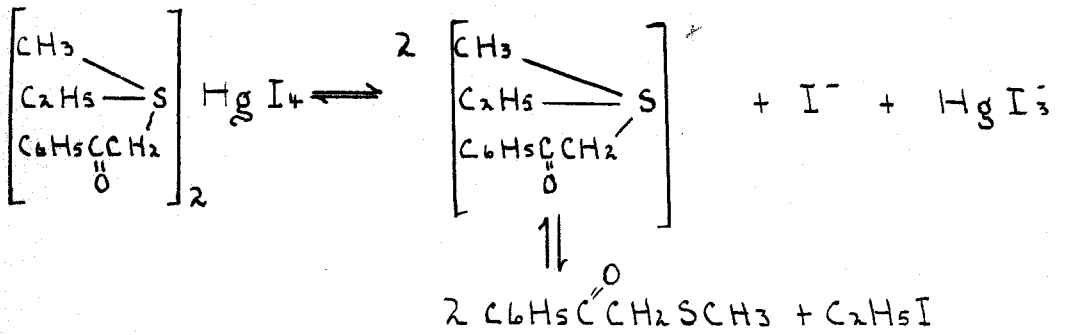
Reychler (79), working with trithioformaldehyde, obtained similar results.

Crum-Brown and Blaikie (11) closely studied the slow, spontaneous decomposition of a series of sulfonium salts. He found the decomposition to take place as would have been predicted by our mechanism.



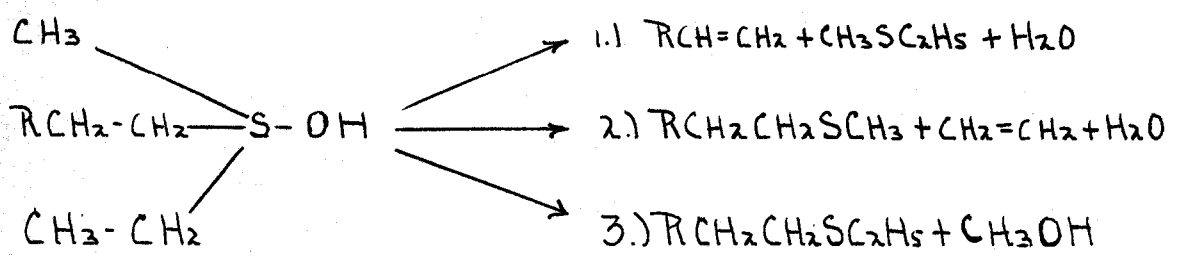


In studying optically active sulfonium derivatives, it has been found that the ready racemization of the mercuri-iodides depends on a reversible decomposition of the ions (80).



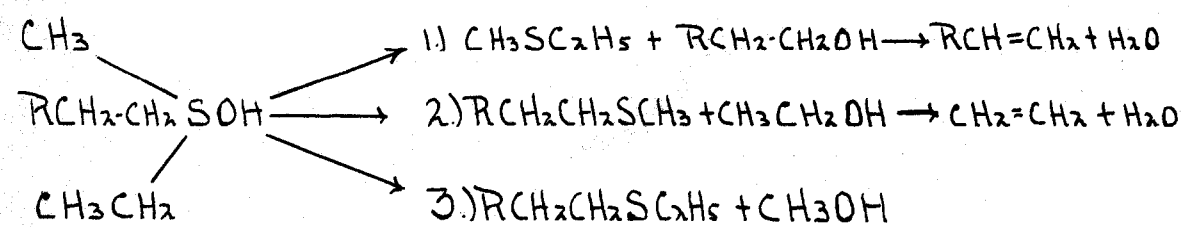
It has not been previously noted, however, that the sulfonium compound can decompose in more than one way.

The thermal decomposition of sulfonium hydroxides has been found by Ingold, Jessop, Kuriyan, Mandour, et al, (25) (80) (81) (82) to take place in three ways, all irreversible.



Similar results were obtained by Brown, Teuffert and Weissbach (83).

This can also be explained by our theory. The sulfonium hydroxide decomposes in three ways instead of two, as in the case of compounds previously described, because the three radicals attached to the sulfur atom are different. The alcohols first formed in 1 and 2 are dehydrated at the



temperature employed, yielding olefines.

IV

NEW DERIVATIVES OF 2-FLUORENE-PHENYL-METHANE

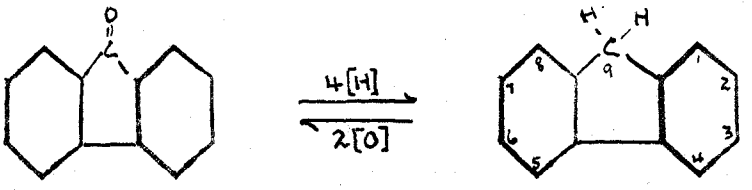
In the course of this investigation, several new derivatives of phenyl-2-fluorene-methane were prepared.

Fluorene was first obtained from the coal tar fraction distilling at 300-340° by Berthelot (84). It showed a very pronounced fluorescence, and, for this reason, he gave it the name, "fluorene". From the heavy tar oils from which naphthalene and anthracene had been separated, Barbier (85) (86) obtained appreciable amounts of the hydrocarbon in a very pure state, melting at 113°. He further showed that its composition is represented by the formula, $C_{13}H_{10}$. However, the beautiful violet fluorescence which had been noted by Berthelot was shown by Hodgkinson and Matthews (87) to be the result of impurities. Pure fluorene crystallizes from benzene, alcohol or glacial acetic acid in colorless shining plates. It may also be obtained in a finely crystalline condition by sublimation.

The melting point of fluorene has been given by most workers as 113°. Others have given 113-114°(88); 113.5-114.5°(89); 114.2°(90); 113-114.5°(91). Its boiling point is given variously as 305°(92); 290-292°; 298°(90). Fluorene is readily soluble in ether, carbon disulfide, benzene and hot alcohol, moderately soluble in chloroform and glacial acetic acid, and sparingly soluble in cold alcohol.

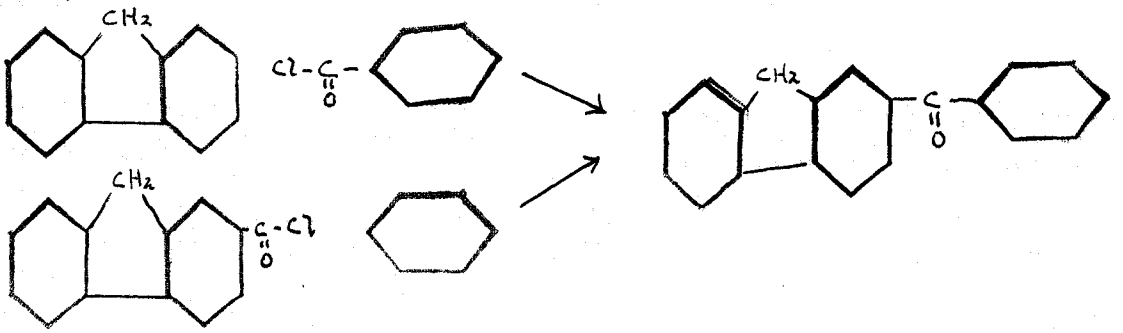
The constitution of fluorene was determined at quite an early date. Fittig (88) and Graebe (93) obtained diphenylene ketone from the calcium salt of 2-2'-carboxy diphenyl, and reduced it to fluorene by distillation with zinc dust. Barbier, Fittig and Schmitz (92) (94) obtained the same compound by oxidizing diphenylene methane, and the former established the

identity of diphenylene methane with the fluorene which Berthelot had obtained from coal tar.



It is immediately evident that, if this structure is correct, the negative character of the two phenylene groups should make the hydrogen attached to the methylene carbon (the 9 position) unusually active, similar to the activity of the hydrogen atoms in malonic ester. This observation is confirmed, since most of the reactions of fluorene involve the 9 position, and consequently the 9 derivatives have been most fully investigated.

The parent substance of the fluorene compounds used in this investigation is 2-fluorene-phenyl ketone. This has previously been prepared both by the action of benzoyl chloride on fluorene, and of fluorene-2-carboxy chloride on benzene. In both cases the reaction takes place at room temperature in carbon disulfide solution, in the presence of anhydrous aluminium chloride (95).



We found, however, that, by using Perrier's modification of the Friedel-Craft reaction, (96) the time required for the preparation was considerably reduced, and the product was much easier to purify.

The 2-benzoyl fluorene forms a phenyl hydrazone and oxime, and is reduced to 2-benzyl fluorene by distillation with zinc dust (95).

2-fluorene-phenyl carbinol has been prepared in this laboratory by the reduction of the ketone with zinc and potassium hydroxide (97). We have found that the reduction can be accomplished as well with zinc and ammonia. In both cases, an alcoholic solution was used. From 2-fluorene-phenyl carbinol, 2-fluorene-phenyl-chloro, bromo, and iodo methane should be obtainable by treatment with the corresponding phosphorus halide. One would expect these halogen derivatives to be more active than the corresponding 9-halogen fluorene, since the combined negative effect of the fluorene and phenyl groups in the former should be greater than that of the two phenylene groups in the latter.

We first attempted to make 2-fluorene-phenyl-bromomethane by the action of phosphorus tribromide on 2-fluorene-phenyl carbinol. A compound was obtained, which was found to melt at 84.5°. This was placed in a bottle, and, after a short time, suddenly decomposed with the evolution of heat. Two compounds were isolated from the fused mass, neither of which contained halogen , and neither of which could be identified (98).

Subsequent attempts to make the bromide and chloride from the carbinol and corresponding phosphorus halide were unsuccessful, and it was believed that the bromide and chloride were so active and unstable that they only could exist for a very short time and under special conditions, if, indeed, they could exist at all.

However, an attempt was made to prepare the bromide by treating 2-fluorene-phenyl carbinol, in glacial acetic acid, with gaseous hydrogen bromide. A compound was precipitated, which, on being freed from the hydrogen bromide and glacial acetic acid fumes, was found to melt at 118°.

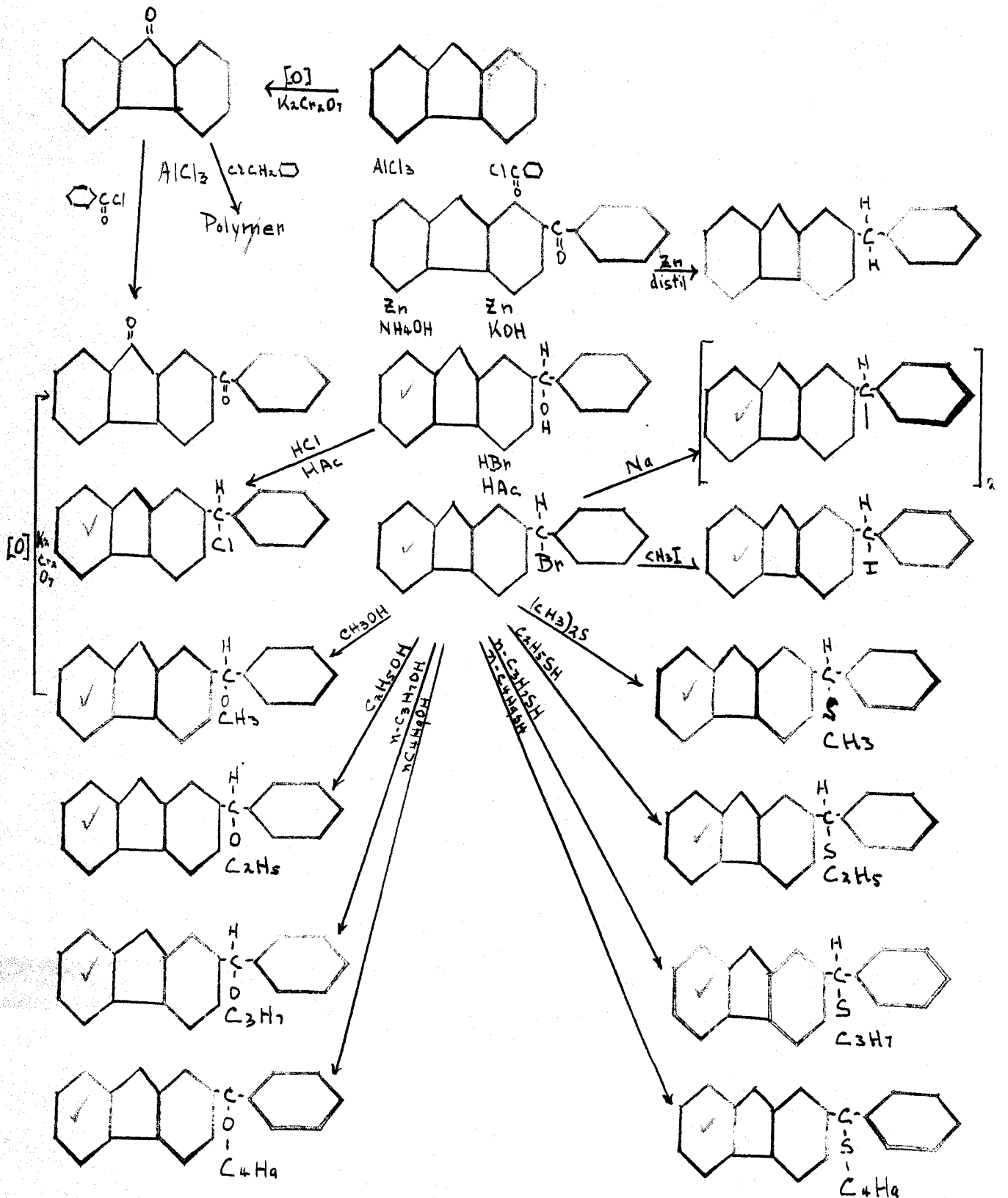
It was found to contain bromide, and an analysis proved it to be the required 2-fluorene-phenyl-bromomethane. The corresponding chloride was obtained in a similar manner, and was found to melt at 120-121°.

An attempt was made to prepare the iodide by treating the bromide with potassium iodide in ether and in acetone solutions. In each case, the solution darkened with free iodine, and only a halogen-free compound melting at 284-5°could be isolated. The same reactants were intimately mixed without a solvent at room temperature and at 90°. In both cases free iodine was liberated, and no compound could be isolated in a pure state.

Finally, the bromide was dissolved in methyl iodide and allowed to stand, protected from moisture with a calcium chloride tube. It was hoped that an equilibrium would be set up with an interchange of bromine and iodine between the methyl group and the 2-fluorene-phenyl-methyl group, and that the methyl bromide would tend to escape as fast as formed, since it is a gas at room temperature. After a few days, a precipitate had formed in the tube. This was filtered off and found to melt at 126-127°. Analysis proved it to be the required iodide.

2-fluorene-phenyl-chloro-, bromo-, and iodomethanes were found to be very active, the activity being in the order of the increasing atomic weight of the halogen atom as anticipated. These compounds react with water, alcohols, and mercaptans with the elimination of hydrogen bromide. With water, the original 2-fluorene-phenyl carbinol is formed. With alcohols, ethers are obtained, and with mercaptans, thioethers.

The iodide is so active that it is difficult to use. The bromide is more active than the chloride, but not as unstable as the iodide. The bro-



✓ compounds not reported in the literature.

mide was therefore used in the preparation of other derivatives.

On boiling a saturated solution of the bromide in methyl alcohol and then cooling, 2-fluorene-phenyl-methoxymethane separates out as white shining plates, melting at 92-93°. It is slightly soluble in methyl and ethyl alcohols, soluble in ether, benzene, chloroform, acetone, and warm glacial acetic acid. On oxidation with potassium dichromate in glacial acetic acid solution, 2-benzoyl fluorenone was formed, m. p. 175-177°. This compound had been previously reported by Fortner (99) (100).

By heating 2-fluorene-phenyl carbinol with ethyl, n-propyl and normal butyl alcohols respectively, 2-fluorene-phenyl-ethoxymethane, m. p. 80.5°; 2-fluorene-phenyl-n-propoxymethane, m. p. 53-54°; and 2-fluorene-phenyl-butoxymethane, m. p. 68-69°, were formed. These compounds are all white crystalline substances and have very similar properties. They are all slightly soluble in methyl and ethyl alcohols, soluble in ether, benzene, chloroform, acetone and warm glacial acetic acid. It will be noted that these ethers show a lowering in their melting points with increasing molecular weights, with a minimum in the propyl derivative. The butyl derivative shows an increase in melting point, and all the higher homologues of this series would probably show a steady increase. An attempt was made to obtain the amyl ether in the same manner, but the compound formed could not be crystallized.

The sulfides corresponding to the ethers were obtained in two ways. The methyl thioether, or (2-fluorene-phenyl-methyl)-methyl sulfide, was obtained by treating 2-fluorene-phenyl-bromomethane with methyl sulfide in sealed tubes at room temperature and at 100°, as previously described

(page 22). It was found to melt at 110°.

This and the other thioethers in this series have properties very similar to those of the corresponding oxyethers. They are slightly soluble in methyl and ethyl alcohols, soluble in ether, benzene, chloroform and acetone.

The next member of this homologous series, 2-fluorene-phenyl-methyl-ethyl sulfide, was prepared by the action of ethyl mercaptan and of sodium ethyl-thiolate on 2-fluorene-phenyl-bromomethane under reflux. The former reaction was found to be more satisfactory than the latter. This is probably because the sodium ethyl-thiolate tends to react with the 9 position of the fluorene nucleus also. The melting point of the compound is 68-70°.

Fluorene-2-phenyl-methyl-n-propyl sulfide was prepared by treating 2-fluorene-phenyl-bromomethane with n-propyl mercaptan at room temperature. The reaction is vigorous. Heat is evolved, hydrogen bromide escapes rapidly, and the reaction mixture becomes a bright red. On heating to complete the reaction, the color disappears when no more hydrogen bromide is evolved. This phenomenon may be due to the intermediate formation of a complex sulfonium salt which is destroyed by heat, or to a color reaction of the fluorene nucleus in the presence of strong acids. It had been observed previously that strong acids cause most fluorene derivatives to develop a red color. The melting point of the fluorene-2-phenyl-methyl-n-propyl sulfide is 51°.

Fluorene-2-phenyl-methyl-n-butyl sulfide was prepared in an analogous manner from 2-fluorene-phenyl-bromomethane and n-butyl mercaptan. The reaction showed a similar violence and development and disappearance of color. The compound melts at 81°.

It will be noted that in this homologous series of sulfides there is a decrease and increase in the melting points, with a minimum at the propyl derivative. This was also pointed out in the case of the corresponding oxyethers.

V

EXPERIMENTAL

PART I: FLUORENE DERIVATIVES

Fluorenone. This compound was prepared according to the method of Huntress, Hershberg, and Cliff (101) by oxidizing fluorene with sodium dichromate.

One hundred grams of unrecrystallized fluorene was placed in a one liter three neck flask equipped with a mechanical stirrer, reflux condenser and dropping funnel. Two hundred cc. of glacial acetic acid was added and the mixture brought to a gentle boil. By means of the dropping funnel, a warm solution of 300 grams of sodium dichromate in a mixture of 400 cc. of glacial acetic acid and 100 cc. of water was added in a steady stream. The reaction mixture was then refluxed for 2½ hours, poured into two liters of ice water, allowed to stand for two hours, and then filtered through a Buchner funnel. The product was washed with water containing enough sulfuric acid to prevent hydrolysis of the chromium salts, and then with pure water.

The bright yellow product was air dried on the filter, placed in a vacuum distillation apparatus, and distilled under reduced pressure. The distillation was stopped when the clear yellow distillate acquired an orange tinge.

The distillate was dissolved in that number of cc. of benzene numerically equal to its weight in grams. To the warm solution was added twice the benzene volume of petroleum ether in such a way that no permanent precipitate of the product formed. This solution was then allowed to stand

until the bright yellow and extraordinarily large crystals of fluorenone had separated. These were filtered with suction, washed with a small quantity of petroleum ether and dried on the filter. Yield 58%. M. P. 83°.

9-fluorenyl alcohol. This compound was obtained from fluorenone according to the method of Werner and Grab (102).

Twenty grams of fluorenone in 50 cc. of 95% ethyl alcohol was mixed with 500 cc. concentrated ammonia (sp. gr. 0.9) and with 30 grams of zinc dust in a one liter three necked flask equipped with a mechanical mercury seal stirrer, a reflux condenser and a gas inlet tube leading to the bottom of the vessel. The reaction mixture was refluxed for approximately 2½ hours while passing in gaseous ammonia from a Dewar flask of liquid ammonia.

The warm solution was filtered from the zinc and allowed to cool in a crystallizing dish. The product, which separated as a jelly-like mat of white needles, was filtered with suction, washed with a small amount of alcohol and dried on the filter. M. P. 152°, which is the same as given by Werner and Grab.

9-fluorenyl bromide. The product obtained in the previous reaction was used without further purification. The alcohol was dissolved in the minimum amount of cold glacial acetic acid in a beaker. Hydrogen bromide, generated from moist red phosphorus and bromine (103), was led into the solution for from five to six hours with stirring. A small amount of white phosphorus in the hydrogen bromide generating flask might be used to initiate the reaction. During this process the white needle-like crystals of the bromide precipitated slowly, and the mixture became warm.

After standing overnight, the crystals were filtered from the fuming

acid mixture and recrystallized from ligroin (boiling from 40-60°). After being filtered with suction and dried on the filter, the product was obtained as a cotton-like mass of long white needles. Melting point 104°, which corresponds to the melting point given in the literature. Yield 26% based on fluorenone.

Fluorenyl-9-dimethyl-sulfonium bromide. This compound was prepared according to the method of Ingold and Jessop (75) using nitromethane as the solvent (104). Instead of dissolving the 9-bromofluorene in nitromethane and then adding methyl sulfide as Ingold and Jessop recommend, it was found that the reaction proceeded much more rapidly and with the use of less nitromethane if the following proceedure were used:

A few grams of the 9-bromofluorene was first dissolved in excess cooled methyl sulfide. Solution takes place very rapidly. Cold nitromethane was then added slowly until the first crystals of fluorenyl-9-dimethyl sulfonium bromide appear. The white granular crystals thereupon form rapidly and almost quantitatively. These were filtered with suction and washed with a small amount of ethyl ether. Melting point 133°, with decomposition. Melting point given by Ingold, 133° .

It was noticed that the compound turned pink on exposure to light, with a lowering of the melting point. It was therefore exposed to subdued light only and stored in suitably protected bottles.

Fluorenyl-9-diethyl-sulfonium bromide. An attempt was made to prepare this compound using the same method as that used for fluorenyl-9-dimethyl sulfonium bromide. No reaction took place, however. The reactants were then mixed with nitromethane as before, placed in a sealed tube, and heated at 100° for eight hours. The mixture was removed from the tube, the liquid evaporated, and the residue extracted with ether. The ether

solution was evaporated, yielding a few long, shining colorless needles of the original bromide, and a reddish amorphous substance which could not be identified.

Dimethyl-sulfonium-9-fluorenylidide (75). One gram of fluorenyl-9-dimethyl-sulfonium bromide was treated with concentrated aqueous ammonia. A light tan precipitate formed immediately. This was filtered off and washed with water, alcohol and ether. The compound quickly turned to a dark red solid on the filter. Melting point 110-112°.

Dilute ammonia and dilute sodium hydroxide were substituted for the concentrated ammonia in additional trials at room temperature and at 0° . In each case a precipitate of shining yellow leaflets formed immediately and quickly turned to a dark red. In most cases the change occurred before the semi-polar compound could be removed from the reaction vessel. Inasmuch as Ingold and Jessop also found that the semi-polar compound is very unstable, no further variations in technique were tried. Instead, it was decided to try the same reaction with other and, possibly, more stable sulfonium compounds.

Ethyl sulfide (105) (106). One half liter of absolute alcohol was gradually added with stirring, over a period of one hour, to a mixture of 250 cc. of fuming and 250 cc. of concentrated sulfuric acid contained in a 1.5 or 2 liter flask. During the addition, the mixture was kept cool at all times by means of an ice bath. The solution was then gradually diluted with ice to about $1\frac{1}{4}$ times its original volume, the solution being well stirred before each further addition of ice. After a final stirring, the solution was slowly poured into three liters of saturated sodium carbonate solution contained in a 5 liter flat bottomed flask. This flask was kept in a crock and surrounded, during the addition, with an ice-salt mix-

ture. The solution was tested with litmus paper from time to time. When it became acid (evolution of carbon dioxide ceased), solid sodium carbonate was added in five to ten gram lots until the solution was again alkaline. The acid mixture and the solid sodium carbonate were then added alternately, a large excess of either being avoided. If, when all the acid mixture had been added, the solution was not alkaline, enough solid sodium carbonate was added to bring it to alkalinity. Approximately 1.5 kilograms of sodium carbonate was required for the neutralization. The addition of the whole of the acid mixture took two to three hours. During the addition, a large quantity of sodium sulfate was formed. This was filtered off with suction on a 12 inch porcelain funnel and washed with small quantities of water, the washings being added to the main portion of the filtrate.

Four hundred grams of potassium hydroxide was dissolved in 800 cc. of water. The solution was divided into two equal portions, and one was saturated with hydrogen sulfide. Both were then mixed.

The filtrate containing the ethyl sodium sulfate, and the alkaline potassium sulfide solution were mixed in a 6 liter R. B. long necked flask, equipped with an empty Hempel fractionating column and water cooled condenser. The mixture was brought to boiling with a hot flame and then distilled at the rate of about 60-80 drops per minute. Due to the formation of small amounts of ethyl mercaptan, the distillation was carried out in a fume chamber. The distillation starts at about 85° , and the temperature gradually rises to about 97° before the ethyl sulfide stops coming over. When, after 2-3 hours, 650 cc. of distillate had been collected, the distillation was stopped and the ethyl sulfide, which comprises the upper layer, was separated by means of a separatory funnel. The yield of crude sulfide at this point was 83 grams. This was dried over-night over 5 grams of anhydrous sodium sulfate and then distilled, the final yield, boiling at 92-93° was

was 75 grams. The last traces of mercaptan can be almost entirely removed with sodium.

2-fluorene-phenyl-ketone. Crude fluorene was recrystallized by boiling 100 grams of fluorene with 250 cc. glacial acetic acid and 20 grams bone black for half an hour, and filtering through a hot water funnel. The white product which crystallized on cooling melted at 114° . Yield 78%.

The ordinary Friedel Crafts reaction and the Perrier modification (96) were used in making the ketone. The latter was much more satisfactory with respect to time required, although it gave slightly smaller yields. Attachment was to the 2-fluorene position as Fortner showed (99) (95) (107).

I. Fifty-five grams of recrystallized fluorene was placed in a liter R.B. flask with three necks. Attached to the flask was a mercury seal stirrer, dropping funnel, and a reflux condenser with calcium chloride tube and alkali trap to remove hydrogen chloride fumes. 350 cc. of anhydrous carbon disulfide and 49 grams of anhydrous aluminium chloride were quickly added, and 50-75 cc. of carbon disulfide used to wash the flask.

Thirty-nine cc. of commercial benzoyl chloride was placed in the dropping funnel with about 80 cc. of carbon disulfide acting as a dilutent.

The material was stirred for about ten minutes before starting to add the benzoyl chloride drop by drop. By adding the benzoyl chloride slowly and taking care that no excess accumulated in the flask, cooling could be avoided. The reaction was controlled by observing the heat evolved and testing the gas from the reflux condenser with ammonium hydroxide.

After all the benzoyl chloride had been added, the mixture was refluxed for about four hours on a water bath. The mixture was then cooled, the supernatant CS_2 poured from the tarry product, and the residue was poured

into a beaker of cracked ice containing 10-20 cc. of hydrochloric acid to dissolve any aluminum chloride or hydroxide. The solid reddish brown mass was steam distilled and the last traces of carbon disulfide and any unreacted benzoyl chloride or benzoic acid removed. Removal of most of the CS_2 before the steam distillation eliminates a good deal of the tarry material. The solid was drained free of water and dried. The brownish yellow porous mass was recrystallized from alcohol. The finely crystalline material is often a pale yellow, but is white when absolutely pure. M. P. 122°. Yield 61%. (99) (97).

II. Ninety-eight grams (.7 mol) of anhydrous aluminium chloride was added over a period of a few minutes to 80.5 cc. (.7 mol) benzoyl chloride in a 2 liter beaker. During the addition, the mixture was stirred as well as possible. This and subsequent operations were performed in a well drawing hood. The mixture became warm and thickened to a stiff brown paste. After all the aluminium chloride had been added, the beaker was heated over a soft luminous flame until the mixture became fluid. Upon cooling in an ice bath, the mixture set to a brown crystalline product.

To the solid aluminium chloride addition product, 560 cc. carbon disulfide was added and the mixture heated on a steam bath with shaking and stirring until the crystalline product was almost entirely dissolved. The usual precautions for handling carbon disulfide were taking during this operation. The solution was then allowed to cool somewhat, and 115 grams of recrystallized fluorene was added with stirring. Quantities of hydrogen chloride were evolved, and it appeared that the reaction was almost

instantaneous. Since no heat was evolved in the reaction, the rate of addition of the fluorene was limited only by the violence of the evolution of the hydrogen chloride.

After all the fluorene had been added, the mixture was heated for a few minutes on the steam bath in order to complete the reaction. It was then cooled in an ice bath and the brown aluminium chloride addition product was filtered with suction and pressed as dry as possible after being washed with a small amount of carbon disulfide.

The residue was then added to 2100 cc. of water containing 140 cc. of concentrated hydrochloric acid. The aqueous suspension of the white crystalline product was then heated to boiling to remove the last traces of carbon disulfide. All of the carbon disulfide has been removed when the solid product sinks to the bottom of the vessel.

The product was then filtered with suction and pressed as dry as possible. At this point the still damp product weighs approximately 230 grams and requires no further drying or purification for use in the preparation of 2-fluorene-phenyl-carbinol. If desired, however, the product can be recrystallized from glacial acetic acid or alcohol. In the latter case, which was sometimes employed, the yield is 58%. M. P. 122°

2-fluorene-phenyl-carbinol. Two methods were used to reduce the 2-fluorene-phenyl-ketone to the carbinol. In the first, zinc and ammonia were employed, and in the second, zinc and potassium hydroxide (97). The latter is recommended because of ease of manipulation.

I. The unrecrystallized and undried 2-fluorene-phenyl-ketone was placed in a two liter beaker and 1200-1500 cc. of 95% alcohol was added. Then 250 cc. of concentrated ammonia solution (sp. gr. 0.9) and 400-500 grams of zinc dust were added. The mixture was stirred mechanically and heated to just below boiling on a hot plate. At the same time, gaseous ammonia was led into the solution from a Dewar flask containing liquid ammonia. Small amounts of alcohol were added to the solution from time to time to maintain its volume. The reaction was complete at the end of about two and a half hours. The hot solution was then filtered from the zinc and allowed to stand until the white crystalline product separated. This comprised the main part of the yield. It was filtered off with suction and the filtrate was treated with water until no more of the carbinol was precipitated. It was found advisable to allow this precipitate to stand for a few hours so that the resultant increase in crystal size would make filtration easier. The product was pure enough to be used in the preparation of 2-fluorene-phenyl-bromo-methane. Yield 82%, based on .7 mol fluorene.

II. The procedure is the same as given in I. except that, instead of concentrated ammonia, 40 cc. of a 25% aqueous solution of potassium hydroxide was added to the alcoholic solution of the ketone, and the reaction mixture was allowed to reflux gently without stirring for seven or eight hours in a three or five liter R. B. flask. Both methods gave approximately the same yields. M. P. 116°.

2-fluorene-phenyl-bromomethane. One hundred and fifty-five grams of the unrecrystallized 2-fluorene-phenyl-carbinol was stirred into a paste with one liter of glacial acetic acid in a two liter beaker in a hood.

Hydrogen bromide gas (103) was then led into the suspension for approximately five hours through an inverted funnel. The mixture became warm and thickened. Care must be taken that the wide end of the funnel does not become clogged with the bromide, as it tends to form a heavy cake as fast as it is formed. The whole mass was stirred as well as possible during the reaction. The saturated hydrogen bromide reaction mixture was allowed to stand overnight in order to complete the reaction, and then the thick paste was filtered with suction and drained as well as possible. Some difficulty was experienced in removing the last traces of hydrogen bromide and glacial acetic acid. This was accomplished most easily by boiling the product with dry ethyl or petroleum ether for about an hour. The white powdery product, only a small amount of which dissolves, was then filtered off with suction and dried on the filter until odorless. Some pure product could also be obtained from the filtrate by partial evaporation. Drying over potassium hydroxide in a vacuum desiccator proved less satisfactory. M. P. 118.5°. Yield 50%, based on .7 mol fluorene.

As this compound was not described in the literature, an analysis was necessary.

Using the sodium fusion method with a Parr bomb (108), the following results were obtained:

Calc. for $C_{20}H_{15}Br$: Br, 23.85. Found: Br, 23.67

The compound was found to be only slightly soluble in ethyl ether, soluble in boiling isopropyl ether. The solubility in the aliphatic hydrocarbons was found to increase with increasing molecular weight and boiling point. It reacts with alcohols and mercaptans, forming ethers and sulfides respectively. It probably also reacts with acetone although no definite

compound could be isolated.

The bromide also reacts with dilute aqueous solutions of alkali forming 2-fluorene-phenyl-carbinol.

2-fluorene-phenyl-chloromethane. I. Three grams of 2-fluorene-phenyl-carbinol were added to 30 cc. of glacial acetic acid. Ten cc. concentrated hydrochloric acid was added to this mixture, which was then warmed gently for a few minutes. After cooling, the precipitate was then filtered off and dried for several days over sodium hydroxide in a vacuum desiccator. M. P. 122° Since this is the same as the melting point of 2-fluorene-phenyl-ketone, a mixed melting point was taken. The melting point of the mixture was found to be 98-112°.

II. Ten grams of 2-fluorene-phenyl-carbinol was dissolved in 150 cc. of glacial acetic acid by warming gently. The heat was removed and hydrogen chloride gas was led in. After about one hour, when the acetic acid had become nearly saturated with the gas, the chloride began to precipitate out. The addition of the gas was continued for another hour, after which time, a heavy, curdy precipitate had formed. This was filtered with suction and then washed twice with petroleum ether (b.p. 30-60°). The white product was then dried on the filter. Melting point of the white powder, 121-122°. Yield 8 grams, 75%.

This compound was analyzed, using the same method as for the bromide. Anal. Calc. for $C_{20}H_{15}Cl$: Cl, 12.22. Found: Cl, 12.19.

The solubilities of this compound were found to correspond closely to those of the bromide. It was found to be much less reactive, and hence less suitable than the bromide for our purpose.

2-fluorene-phenyl-iodomethane. Three grams of 2-fluorene-phenyl-

bromomethane was dissolved in excess methyl iodide and allowed to stand, protected from moisture with a calcium chloride drying tube. After a few days a precipitate had formed. This was filtered off and found to melt at 126-127°.

Anal. Calc. for $C_{20}H_{15}I$: I, 33.2 Found: I, 32.5

Three grams of 2-fluorene-phenyl-bromomethane was allowed to stand with five grams of potassium iodide and 60 cc. of acetone for several days at room temperature.

Free iodine was liberated and a finely divided precipitate was formed which was easily separated from the heavier potassium iodide crystals by shaking and decanting the suspension of the precipitate. The acetone suspension was then filtered and the precipitate was washed with water to remove any potassium iodide remaining. The compound melted at 284-285° and gave no test for halogen. It was found to be identical with one of the compounds obtained from the Wurtz synthesis of sym-di-2-fluorene-diphenyl ethane (page 59).

2-fluorene-phenyl-methoxymethane. Twenty-five cc. of methyl alcohol at its boiling point was saturated with 2-fluorene-phenyl-bromomethane and the solution refluxed for half an hour. It was then allowed to cool, whereupon the product precipitates as shining white plates. Melting point 92-93°. This compound was found to be slightly soluble in cold methyl and ethyl alcohols, soluble in acetone, chloroform, ether and glacial acetic acid.

Anal. Calc. for $C_{21}H_{18}O$: C, 88.06; H, 6.34.

Found: C, 88.33; H, 6.33.

A few grams of 2-fluorene-phenyl-methoxymethane was dissolved in

warm glacial acetic acid and treated with potassium dichromate. The mixture was refluxed for half an hour and then poured into about 300 cc. of water. This was then filtered and the residue recrystallized from a 50% mixture of alcohol and ether. The bright yellow crystalline compound which was obtained proved to be 2-benzoyl-fluorenone by its melting point, 177°, and mixed melting point.

2-fluorene-phenyl-ethoxymethane. A small amount of 2-fluorene-phenyl-bromomethane was boiled with excess ethyl alcohol. The white crystalline precipitate which was formed was filtered off. Test for halogen negative. Melting point, 80-80.5°. Slightly soluble in methyl and ethyl alcohols. Soluble in acetone, chloroform, ether, and benzene.

Anal. Calc. for $C_{22}H_{20}O$: C, 87.94; H, 6.72.

Found: C, 88.06; H, 6.52.

2-fluorene-phenyl-n-propoxymethane. Boiling n-propyl alcohol was saturated with 2-fluorene-phenyl-bromomethane and allowed to cool. On standing over-night, the mixture set to a stiff mat of white needles. These were filtered off, washed with petroleum ether and dried. Their indefinite melting point indicated that they were impure. They were therefore dissolved in ether, and alcohol was added to a faint cloudyness. On standing, white needles separated, melting point, 53-54°. The compound is slightly soluble in ethyl and methyl alcohols, soluble in benzene, chloroform, acetone and ether.

Anal. Calc. for $C_{23}H_{22}O$: C, 87.84; H, 7.06.

Found: C, 88.26; H, 7.16.

2-fluorene-phenyl-n-butoxymethane. A few grams of 2-fluorene-phenyl-

bromomethane was dissolved in redistilled n-butyl alcohol and refluxed for two hours. After standing over-night, the brown solution was filtered and the excess butyl alcohol removed as completely as possible by distillation. The residue was then heated for about an hour at 100° under reduced pressure. The still liquid residue was dissolved in ether, boiled with bone black, and filtered. The residue was still liquid on evaporating the ether. It was redissolved in ether and enough alcohol added to bring about a faint cloudyness. The solution was then allowed to evaporate slowly. A white crystalline substance, melting point, 68-69°, was deposited. The compound was found to be slightly soluble in methyl and ethyl alcohol, soluble in acetone, benzene, chloroform and ether.

Anal. Calc. for $C_{24}H_{24}O$: C, 87.74; H, 7.37
Found: C, 88.20; H, 7.47.

(2-fluorene-phenyl-methyl)-ethyl sulfide. A few grams of 2-fluorene-phenyl-bromomethane was refluxed with excess ethyl mercaptan for several hours. Hydrogen bromide and some bromine were evolved. The excess ethyl mercaptan was evaporated and the residue dissolved in hot alcohol. The sulfide precipitated as an oil on cooling, but upon standing for several days with the mother liquor, crystallization gradually occurred. The white crystals melted at 68-70°. They were found to be slightly soluble in ethyl and methyl alcohols, soluble in ether, chloroform and benzene.

Anal. Calc. for $C_{22}H_{20}S$: S, 10.20; Found: S, 10.13.

An attempt was made to prepare the same compound by using sodium ethylmercaptolate instead of ethylmercaptan. The same procedure was followed as in the previous trial. In this case, however, a sulfur containing compound was obtained which melted at 58-60°. A mixed melting point with the sulfide obtained previously showed no lowering. Since

analysis showed a sulfur content equal to that of the sulfide with two molecules of ethyl alcohol, attempts were made to drive off any alcohol of crystallization with heat. In all cases, a gum was obtained which could not be crystallized.

Anal. Calc. for $C_{22}H_{20}S.2\ C_2H_5OH$: S, 7.83; Found: S, 7.68, 7.71.

2-fluorene-phenyl-methyl n-propyl sulfide. Excess n-propyl mercaptan was added to a few grams of 2-fluorene-phenyl-bromomethane at room temperature. An immediate evolution of hydrogen bromide occurred and a bright red color developed. The mixture was then refluxed for about a half an hour, until the evolution of hydrogen bromide ceased and the red color disappeared. The excess n-propyl mercaptan was then evaporated and the residue dissolved in ether, boiled with bone black and filtered. An equal volume of ethyl alcohol was added and the solution allowed to evaporate slowly at room temperature. After several days, the white, needle-like crystals of the n-propyl sulfide precipitated. Melting point 51° . This compound was found to be slightly soluble in methyl and ethyl alcohols, soluble in ether, benzene, chloroform and acetone.

Anal. Calc. for $C_{23}H_{22}S$: S, 9.69 . Found: S, 9.73 .

2-fluorene-phenyl-methyl n-butyl sulfide. 2-fluorene-phenyl-bromomethane was treated with excess n-butyl mercaptan at room temperature. Hydrogen bromide was evolved immediately and a bright red color developed. The mixture was refluxed for about a half an hour, until hydrogen bromide was no longer evolved and the red color disappeared. The excess butyl mercaptan was evaporated and the residue was dissolved in ether and filtered. Alcohol was added until a slight precipitation

occurred. The white crystalline sulfide separated on standing over-night. Melting point 81° . Soluble in ether, benzene, chloroform and acetone. Slightly soluble in methyl and ethyl alcohols.

Anal. Calc. for $C_{24}H_{24}S$: S, 9.29. Found: S, 9.26.

Benzyl-2-fluorene. Sixteen grams of fluorenone was dissolved in one hundred cc. of carbon disulfide in a 3 necked flask containing 12 grams of anhydrous aluminium chloride and equipped with a mercury seal stirrer, reflux condenser and dropping funnel. 10.4 cc. of benzyl chloride was added over a period of one half an hour. During the addition, the reaction mixture was cooled in an ice bath. After allowing the mixture to come to room temperature slowly, it was refluxed for two and a half hours. The hydrogen chloride fumes which were evolved were absorbed in an alkali trap.

After standing over-night, the aluminium chloride addition product was decomposed with ice and dilute hydrochloric acid. The reaction mixture was then transferred to a steam distillation apparatus and the carbon disulfide removed with steam.

The product was filtered with suction and dried on the filter. After being boiled with benzene to remove the unreacted fluorenone, the undissolved product was again filtered with suction and dried. Yield 55%. The compound was found not to melt, but to carbonize around 274° .

This compound was found to be practically insoluble in all organic solvents. Among those tried were, benzene, alcohol, ether, petroleum ether, chloroform, carbon tetrachloride, nitromethane, nitrobenzene, pyridine and acetanilide. Since it was also insoluble in molten camphor, a molecular weight determination was out of the question.

An attempt was made to reduce this supposed ketone to the corresponding alcohol by heating it for several days with zinc and potassium

hydroxide in ethyl alcohol. Very little, if any, reaction took place. The zinc and insoluble compound were filtered from the alcohol, and the zinc was removed with dilute hydrochloric acid. The supposed ketone was recovered quantitatively. The fact that, upon treating the alcoholic filtrate with water, a very slight turbidity was obtained, indicated that the reaction might have proceeded to a very slight extent.

Anal. Calc. for $C_{20}H_{14}O$: C, 88.86; H, 5.22.

Found: C, 94.61; H, 6.7.

Since the analysis indicates that the compound is obviously a hydrocarbon, it was supposed that polymerization had occurred with the elimination of water. This view is enhanced by the unusual insolubility of the compound, its inertness to various reagents, including concentrated sulfuric and nitric acids, and its lack of melting point.

Sym-di-2-fluorene-di-phenyl-ethane. Ten grams of sodium, five grams of 2-fluorene-phenyl-bromomethane, and 200 cc. of ether were placed in a flask and refluxed for twenty-four hours. The excess sodium was removed and the solid which had precipitated was filtered off and washed with water to remove the sodium bromide. The solid was then dried and found to melt at 168°. A mixed melting point proved this to be identical with the compound obtained from the decomposition of 2-fluorene-phenyl-iddomethane (page 64).

The ether solution was evaporated at room temperature, giving a clear sirupy residue. This was boiled with alcohol, in which it is not appreciably soluble, and on decanting the alcohol it appeared to be much harder and more brittle. It was then dissolved in boiling benzene, in

which it is very soluble. It did not crystallize out on cooling, so the benzene was allowed to evaporate. The residue was a tar. This was then dissolved in acetone, and a white, crystalline substance precipitated on partial evaporation. Melting point, 274-280°. A mixed melting point with the substance (m. p. 284°) which had been obtained from the reaction of potassium iodide with 2-fluorene-phenyl-bromomethane indicated that these two substances are identical. The mixed melting point was found to be 282-284°.

The existence of the sym-di-2-fluorene-di-phenyl ethane in two diastereoisomeric forms is to be expected since it has two asymmetric carbon atoms, each having the same groups. The two diastereoisomers are, a meso and a racemic form.

PART II: DECOMPOSITION OF SULFONIUM SALTS

Dimethyl-2-fluorene-benzyl-sulfonium bromide. I. 2-fluorene-phenyl-bromomethane was treated with excess dimethyl sulfide, and the solution was warmed for fifteen minutes. On evaporating the dimethyl sulfide, a cream colored substance was obtained which turned pink and then red in the space of about ten minutes. It melted at 112-116° with the evolution of dimethyl sulfide. A mixed melting point with the bromide was taken and showed no change.

II. A few grams of 2-fluorene-phenyl-bromomethane was dissolved in nitromethane by warming on the water bath. After cooling, an excess of dimethyl sulfide was added and the vessel was stoppered and allowed to stand for a few days. Upon examination, it was noted that a few large crystals had formed. These were carefully removed and found to melt at 195-196°. This corresponds to the melting point of trimethyl sulfonium

bromide. The filtrate was evaporated and an amorphous residue was obtained, which softened between 50°and 60° .

III. One gram of 2-fluorene-phenyl-bromomethane was treated with two cc. (excess) dimethyl sulfide, dissolved in nitromethane in a tube, and the tube sealed. The tube was heated at 100° for two and a half hours and then allowed to stand over-night. On opening the tube, a mat of long shining needles was found (2.5 gm.). M. P. 195-200°. Qualitative test for sulfur and halogen was positive. Anal. Calc. for $(CH_3)_3SBr$: Br, 50.89. Found: Br, 50.59.

IV. Stoichiometric quantities of 2-fluorene-phenyl bromomethane (2.7 gm.) and dimethyl sulfide (.5 gm.) were dissolved in nitromethane. The mixture was heated for eight hours at 100°in a sealed tube. After standing over-night, two distinct precipitates were noted and removed by filtration. One of these was a brown solid in small lumps, and the other consisted of large well-formed colorless crystals like those obtained in the previous sealed tube trials and which were identified as $(CH_3)_3SBr$. The mixture was then extracted with warm water and filtered. On carefully evaporating the filtrate, the rest of the trimethyl sulfonium bromide, II, was obtained.

The brown residue from the extraction was dissolved in hot alcohol, filtered from a small amount of gum and the solution evaporated to dryness. The light brown residue (III) melted at 248-250°. It gave a positive test for halogen but no test for sulfur.

The filtrate from the original reaction mixture was evaporated to a black gummy mass. This was dissolved in ether, warmed with bone black,

cooled and filtered. A very small amount of a grey powder (I) was obtained on evaporating the filtrate. Qualitative tests for sulfur and halogen were positive. The gummy residue, still mixed with the bone black, was boiled with alcohol and filtered. Upon cooling the filtrate, a white crystalline precipitate (IV) was formed. M.P. 88-90°. Qualitative tests for sulfur and halogen were negative.

TABLE I

TABLE OF SUBSTANCES ISOLATED FROM REACTIONS IV AND V

Cpd.#	M.P.	Sulfur	Halogen	Identified as:
I	225-235	None	None	
II	178	Positive	Positive	$(CH_3)_3SBr$
III	248-250	None	24.02%	
IV	88-90	None	None	
V	105	None	None	

V. One gram of 2-fluorene-phenyl bromomethane and 3 cc. (excess) dimethyl sulfide were dissolved in 10 cc. of nitromethane in a tube which was then sealed. This was heated for eight hours at 100°. After standing over-night the tube was opened and trimethyl sulfonium bromide (II) was found as the only precipitate. This was filtered off and the nitromethane and excess dimethyl sulfide was evaporated from the filtrate. The residue so obtained was dissolved in ethyl alcohol, heated with bone black and the hot solution filtered. A white crystalline compound (V) precipitated on cooling the filtrate. This was removed and dried on filter paper. M.P. 105°. Qualitative tests for sulfur and halogen were negative.

In view of the number of compounds and the inconsistant results obtained, it was thought probable that the nitromethane was acting as a methylating agent. In subsequent runs, therefore, the nitromethane

was omitted.

VI. (2-fluorene-phenyl-methyl)-methyl sulfide. Three grams of 2-fluorene-phenyl-bromomethane and 10 cc. of dimethyl sulfide were heated in a sealed tube at 100° for six and a half hours. On opening the tube, a precipitate was obtained which was filtered off. The residue was extracted with warm water and the aqueous solution evaporated. The residue remaining after evaporation melted at 200° and gave no test for sulfur or halogen. Anal. Calc. for $(CH_3)_3SBr$: Br, 50.89. Found: Br, 51.00, 51.07.

The residue from the extraction with water was crystallized by dissolving it in hot alcohol and allowing the alcoholic solution to cool. A gum precipitates which crystallizes if allowed to stand with the supernatant liquid for several days. This was the only way a crystalline product could be obtained, although the compound was also soluble in ether, benzene and acetone. M.P. 109.5° Anal. Calc for $C_{21}H_{18}S$: S, 10.59. Found: S, 10.48.

VII. A few grams of (2-fluorene-phenyl-methyl)-methyl sulfide was heated in a sealed tube at 100° with excess methyl iodide for six hours. After cooling, the tube was opened and the liquid portion decanted. The small amount of solid remaining was extracted with water. This was recovered by evaporation and then recrystallized from water. The long needle-like crystals melted at 180°. Because of the fact that the sodium fusion method of analysis used too much time, this and subsequent analyses for halogen in water soluble compounds were made by titrating with standard silver nitrate with potassium chromate as an indicator (109). Anal. Calc. for $(CH_3)_3SI$: I, 64.13. Found: I, 63.02.

The liquid portion, which had been decanted from the trimethyl

sulfonium iodide, was evaporated. The residue appeared to contain an appreciable quantity of free iodine. This was extracted with hot alcohol, leaving a small amount of a white crystalline compound which melted at 160°. This was believed to be sym-di-2-fluorene-diphenyl ethane and to have resulted from the decomposition of 2-fluorene-phenyl-iodomethane. Qualitative tests for sulfur and halogen were both negative.

VIII. Eight tenths of a gram of 1,1-fluorene-2-phenyl dimethyl sulfide and 5 cc. (excess) methyl iodide were placed in a sealed tube and allowed to stand at room temperature protected from light. At the end of about five hours a slight precipitate was noticed. At the end of twenty-four hours a very appreciable quantity of precipitate had formed. The tube was opened and the precipitate quickly filtered off with suction. It was then dissolved in cold water, filtered, and recovered by evaporation. M.P. 203° . Anal. Calc for $(CH_3)_3SI$: I, 64.13. Found: I, 65.63.

The methyl iodide solution which had been removed from the tube was allowed to evaporate. A residue was obtained which contained so much iodine that it was impossible to isolate any other compound in a reasonably pure state.

IX. Five cc. of ethyl sulfide and three grams of 2-fluorene-phenyl-bromomethane were heated at 200° for 48 hours in a sealed tube and then allowed to stand at room temperature for several days. The tube was opened and the excess diethyl sulfide was evaporated at room temperature. The black residue showed evidence of considerable carbonization. It was extracted with absolute alcohol and filtered. The alcohol was evaporated

and a slightly discolored product was obtained. M.P. 80°. This melting point and a mixed melting point showed it to be 2-fluorene-phenyl-ethoxy-methane, indicating that the bromide had not reacted with the ethyl sulfide. This result was in accordance with that obtained with the 9-fluorenyl bromide and ethyl sulfide.

X. Five grams of (2-fluorene-phenyl-methyl)-methyl sulfide and 2.13 grams of methyl iodide (stoichiometric quantities) were placed in a test tube which was stoppered and sealed with paraffin. After standing for several days, the solid which had separated was filtered off, extracted with water and the water evaporated. A white crystalline compound was obtained. M.P. 200°. Anal. Calc for $(CH_3)_3SI$: I, 64.13. Found: I, 63.06.

The residue left after the extraction with water was found to melt at 160°. This corresponds to the melting point of the compound obtained in VII and believed to be sym-di-2-fluorene-diphenyl-ethane resulting from the decomposition of 2-fluorene-phenyl-iodomethane.

XI. One gram of (2-fluorene-phenyl-methyl)-methyl sulfide was placed in a sealed tube with excess ethyl iodide and heated at 100° for fifteen hours. After standing at room temperature over-night, a small amount of a dark solid containing a few colorless crystals was found at the bottom of the tube. The supernatant liquid was decanted from the solid and evaporated to dryness. The residue was a dark cohesive mass evidently containing a considerable quantity of iodine.

The solid remaining in the tube was washed with water, in which it seemed only slightly soluble, and then with sodium thiosulfate solution to remove the iodine. The solid remaining was crystalline in appearance, a light olive green in color, and melted at 100-105° with no apparent

decomposition.(5) Anal. Calc for $(C_2H_5)_2CH_3SI$: I, 54.54. Found: I, 53.09.

XII. Four grams of(2-fluorene-phenyl-methyl)-methyl sulfide and excess ethyl bromide were heated at 100° in a sealed tube for sixteen hours. On opening the tube, the (2-fluorene-phenyl-methyl)-methyl sulfide was recovered unchanged.

XIII. Quantitative run. 0.846 grams of dimethyl sulfide and 4.56 grams of 2-fluorene-phenyl-bromomethane (equimolar quantities) were heated at 100° in a sealed tube for fourteen hours. The tube was opened and the solid was removed and boiled with methyl alcohol for half an hour in order to convert any unchanged bromide to the methyl ether. The methyl alcohol was evaporated and the residue was extracted with water. The trimethyl sulfonium bromide dissolved. The water extract was evaporated and the sulfonium bromide weighed. The residue from the aqueous extraction was heated for a short time with an excess (11 grams) of mercuric chloride, in alcohol solution, to form the mercuric chloride addition product of (2-fluorene-phenyl-methyl)-methyl sulfide. The alcohol was evaporated and the residue extracted with ether. The ether extract was evaporated and the 2-fluorene-phenyl-methoxy-methane together with the excess mercuric chloride was obtained. The residue from the ether extraction consisted of the mercuric chloride addition product. The quantitative results of this critical experiment are given in Table II.

The mercuric chloride addition product was found to melt at 128°. It is soluble in ether and slightly soluble in alcohol.

TABLE II

Quantitative Results of XIII

Starting substances:

Dimethyl sulfide . . . . . 0.846 gm.; 0.0136 mol.
2-fluorene-phenyl-bromomethane . . 4.56 gm.; 0.0136 mol.

Products:	Calc. gm.	Found gm.
(2-fluorene-phenyl-methyl)-methyl sulfide, mercuric chloride . .	4.01	4.01
trimethyl-sulfonium bromide	1.07	1.10
2-fluorene-phenyl-methoxy-methane . .	1.95	2.13

VI

SUMMARY

A mechanism has been proposed for the decomposition of sulfonium salts which explains the hitherto imperfectly understood course of reactions between organic sulfides and organic halides. The mechanism postulates that, in all such reactions, a sulfonium salt is first formed. This can then decompose in one, two or three ways, depending on the complexity of the salt, to give halides and sulfides, which, in turn, can combine to form the same or other sulfonium salts. The tendency is for thatsulfonium salt having the smallest organic radicals, and consequently the greatest stability, to be the final product of the reaction.

In the course of this investigation, the following new compounds were prepared:

Name	Formula	Melting Point °C.
2-fluorene-phenyl-bromomethane	$C_{20}H_{15}Br$	118.5
2-fluorene-phenyl-chloromethane	$C_{20}H_{15}Cl$	122
2-fluorene-phenyl-iodomethane	$C_{20}H_{15}I$	126-7
2-fluorene-phenyl-methoxy-methane	$C_{21}H_{18}O$	92-3
2-fluorene-phenyl-ethoxy-methane	$C_{22}H_{20}O$	80.5
2-fluorene-phenyl-n-propoxy-methane	$C_{23}H_{22}O$	53-4
2-fluorene-phenyl-n-butoxy-methane	$C_{24}H_{24}O$	68-9

(2-fluorene-phenyl-methyl)-methyl sulfide	$C_{21}H_{18}S$	110
(2-fluorene-phenyl-methyl)-ethyl sulfide	$C_{22}H_{20}S$	68-70
(2-fluorene-phenyl-methyl)-n-propyl sulfide	$C_{23}H_{22}S$	51
(2-fluorene-phenyl-methyl)-n-butyl sulfide	$C_{24}H_{24}S$	81
sym-di-2-fluorene-di-phenyl ethanes	$C_{40}H_{30}$	meso 168 racemic 274-80

BIBLIOGRAPHY

1. Oefele, Ann. Chem. Pharm., 132, 83, (1864).
2. Cahours, Ann. Chem. Pharm., 135, 354, (1865).
3. Cahours, Compt. Rend., 60, 620, 1174, (1865).
4. Cahours, Compt. Rend., 81, 1163, (1875).
5. Cahours, Compt. Rend., 80, 1317, (1875).
6. Cahours, Ann. Chem. Pharm., 136, 75, (1865).(?)
7. Scholler, Ber., 7, 1274, (1874).
8. Kruger, J. pr. Chem., (ii), 14, 207, (1876).
9. Dehn, J. pr. Chem., (ii), 14, 108, (1876). (?)
10. Dehn, Ann., IV, Suppl., 83, (1865-1866).
11. Crum-Brown and Blaikie, J. pr. Chem., (2), 23, 395-401, (1881).
12. Ferrer, Annales soc. espan. fis. quim., 16, 724-7, (1918).
13. Klinger, Ber., 10, 1880, (1877).
14. Renshaw, Bacon and Roblyer, J. Chem. Soc., 48, 517-20, (1926).
15. Ettel and Kohlik, Collection Czechoslov. Chem. Communications, 3, 585-92, (1931).
16. Bennett and Hock, J. Chem. Soc., 127, 2671-7, (1925).
17. Bennett and Hock, J. Chem. Soc., 130, 2496-9, (1927).
18. Smiles, Proc. Chem. Soc., 21, 92-93, (1905).
19. Delisle, Ber., 25, 2450, (1892).
20. Chichibabin, Fr. Pat., 769216, Aug. 22, 1934.
21. Chichibabin and Besteizhev, Compt. rend., 200, 242-4, (1935).
22. Davies, Ber., 24, 3548, (1891).
23. Steinkopf and Muller, Ber., 56B, 1926-30, (1923).

24. Wegscheider and Schreiner, Monatsh., 40, 325, (1919).

25. Hughes and Ingold, J. Chem. Soc., 136, 1571, (1933).

26. Smiles, Trans. Chem. Soc., 77, 163, (1900).

27. Hilditch and Smiles, J. Chem. Soc., 91, 1394-99, (1907).

28. Meyer and Jacobson, "Lehrbuch der Organische Chemie", 1920, Vol. II, p. 30.

29. Kehrmann and Duttenhofer, Ber., 38, 4197, (1905).

30. Kehrmann and Dardel, Ber., 55, 2346, (1922).

31. Sachs and Ott, Monatsh., 47, 415, (1926).

32. Michaelis and Godchaux, Ber., 24, 757-64, (1891).

33. Smiles and Le Rossignol, Proc. Chem. Soc., 22, 24, (1906).

34. Smiles and Le Rossignol, Chem. Soc. Trans., 89, 696-708, (1906).

35. Courtot and Tung, Compt. rend., 200, 1541-3, (1935).

36. Courtot and Chiffert, Compt. rend., 194, 986-8, (1932).

37. Courtot and Tung, Compt. rend., 197, 1227-9, (1933).

38. Courtot and Freukiel, Compt. rend., 199, 557-9, (1934).

39. Libermann, Compt. rend., 197, 1425-7, (1933).

40. Smiles and Le Rossignol, Proc. Chem. Soc., 22, 158, (1906).

41. Schönberg and Stephenson, Ber., 66B, 250-2, (1933).

42. Hinsberg, Ber., 62B, 127-35, (1929).

43. Hinsberg, Ber., 69B, 492-5, (1936).

44. Klason, Ber., 37, 1349-60, (1904).

45. Patein, Bull. soc. chim., (3), 3, 164-71, (1890).

46. Patein, Bull. soc. chim., (2), 49, 678, (1888).

47. Patein, Compt rend., 106, 861-3, (1888).

48. Russel, Cozalet and Irvin, J. Chem. Soc., 135, 841-51, (1932). (?)

49. Ray, Adhikari and Ray, J. Indian Chem. Soc., 8, 251-5, (1931).

50. Blätter, Monatsh., 40, 417-29, (1920).

51. Steinkopf and Teichmann, J. pr. Chem., 127, 337-56, (1930).

52. Bayer and Co., D.R.P., 97207.

53. Steinkopf and Bessartsch, J. pr. Chem., 109, 230-64, (1925).

54. Steinkopf, Roch and Schultz, J. pr. Chem., 113, 159-65, (1926).

55. Dobbin and Masson, J. Chem. Soc. Trans., 47, 56-68, (1885).

56. Nasini and Scala, Gazzetta, 18, 67, (1888).

57. Klinger and Maassen, Ann., 243, 193, (1888).

58. Klinger and Maassen, Ann., 252, 241, (1889).

59. Brjuchonenko, Ber., 31, 3176, (1899).

60. Stromholm, Ber., 33, 823-41, (1900).

61. Pope and Peachey, Trans. Chem. Soc., 77, 1072, (1900).

62. Pope and Peachey, Proc. Chem. Soc., 16, 12, (1900).

63. Smiles, J. Chem. Soc. Trans., 87, 450-61, (1905).

64. Smiles, J. Chem. Soc. Trans., 77, 1174, (1900).

65. Smiles and Hilditch, Proc. Chem. Soc., 23, 35-36, (1907).

66. Wedekind, Ber., 58B, 2510-18, (1925).

67. Hilditch and Smiles, (?) Trans. Chem. Soc., 47, 56, (1885).

68. Cavel and Sugden, J. Chem. Soc., 77, 2572-9, (1900).

69. Ray and Adhikary, J. Indian Chem. Soc., 7, 297-303, (1930).

70. Kenyon and Phillips, J Chem. Soc., 127, 2552, (1925).

71. Harrison, Kenyon, and Phillips, J. Chem. Soc., 129, 2079, (1926).

72. Langmuir, J. Am. Chem. Soc., 42, 274-92, (1920).

73. Kehrmann and Duttenhofer, Ber., 38, 4197, (1905).

74. Kehrmann and Dardel, Ber., 55, 2346, (1922).

75. Ingold and Jessop, J. Chem. Soc., 1930, 715.

76. Hughes and Kuriyan, J. Chem. Soc., 1935, 1609-11.

77. Private communication, Ray and Palinchak.

78. Platonov and Anisimov, J. Gen. Chem. (U.S.S.R.), 5, 622-4, (1935).

79. Reychler, Bull. soc. chim., (3), 33, 1226-32, (1905).

80. Ingold, Jessop, Kuriyan and Mandour, J. Chem. Soc., 1930, 2107.(?)

81. Gleave, Hughes and Ingold, J. Chem. Soc., 1935, 236-44.

82. Ingold and Kuriyan, J. Chem. Soc., 1933, 991-3.

83. Brown, Teuffert and Weissbach, Ann., 472, 121-42, (1929).

84. Berthelot, Ann. Chim. Phys., (4), 12, 222, (1867).

85. Barbier, Compt. rend., 77, 442, (1873).

86. Barbier, Ann. Chim. Phys., (5), 7, 472, (1886).

87. Hodgekinson and Matthews, Chem. Soc. Trans., 43, 163, (1883).

88. Fittig, Ber., 6, 187, (1873).

89. Weger and Doring, Ber., 36, (1903).

90. Worleiner and Murphy, Ind. Eng. Chem., 15, 1140, (1923).

91. Everest, "Higher Coal Tar Hydrocarbons", Longmans, Green and Co., 1927, p.63.

92. Barbier, Compt. rend., 79, 1151, (1874).

93. Graebe, Ber., 7, 1625, (1874).

94. Fittig and Schmitz, Ann., 193, 134, (1878).

95. Fortner, Monatsh., 23, 921, (1902).

96. Perrier, Bull. Soc. Chim., (3), 31, 859, (1904).

97. Harrold, "Preparation of 2-fluorene-phenyl-nitromethane", Ph. D. Thesis, 1934, University of Cincinnati.

98. Levine, "Decomposition of 2-fluorene-phenyl-bromo-, and chloro-methanes", M.A. Thesis, 1936, University of Cincinnati.

99. Fortner, Monatsh., 25, 443, (1904).

100. Fortner, Monatsh., 23, 921, (1902).

101. Huntress, Hershberg and Cliff, J. Am. Chem. Soc., 53, 2720, (1931).

102. Werner and Grab, Ber., 37, 2896, (1904).

103. Partington, "Textbook of Inorganic Chemistry", Macmillan, 4th edition, p. 356.

104. Richardson and Soper, J. Chem. Soc., 1929, 1873.

105. Hobson, Ann., 102., 75, (1857).

106. Klason, Ber., 20, 3413, (1887).

107. Gotz, Monatsh., 23, 27, (1902).

108. Parr Instrument Co., Moline, Ill., Booklet 113.

109. Hall, "Textbook of Quantitative Analysis", p. 120, John Wiley and Sons, 1930.