m.p. 221–222°) was heated under reflux with zinc (2.0 g.) and aqueous potassium hydroxide (40 ml. 10%) for 8 hr. The cooled reaction mixture was filtered to remove excess zinc and acidified. A white precipitate (0.3 g.) settled out which melted over a range 190–208°. Three crystallizations from benzene raised the melting point to 209–209.5°. A mixed melting point with 5-methoxy-6-hydroxyphthalide (II) obtained by demethylation of metameconine showed no depression.

5-Methoxy-6-acetoxyphthalide. 5-Methoxy-6-hydroxyphthalide (II) was acetylated with acetic anhydride in the usual way to give the acetyl derivative with a melting point of 184–186° which was raised to 186–186.6° by two crystallizations from dilute acetic acid (1:1).

Anal. Calcd. for $C_{11}H_{10}O_5$: C, 59.46; H, 4.54; $-OCH_3$, 13.96. Found: C, 59.77, 59.44; H, 4.50, 4.52; $-OCH_3$, 13.96.

5-Hydroxy-6-methoxyphthalide (XVI). 4-Bromo-5-hydroxy-6-methoxy-phthalide (XII) (0.2 g., m.p. 246–247°) was debrominated with zinc (1.0 g.) and aqueous potassium hydroxide (20 ml. 10%) by the method above for 5-methoxy-6-hydroxyphthalide. The product after three crystallizations from benzene melted at 177–177.6°.

Anal. Calcd. for $C_9H_8O_4$: C, 59.98; H, 4.48. Found: C, 60.04; H, 4.35.

The infrared spectrum was very similar to the spectrum of the isomeric 5-methoxy-6-hydroxyphthalide (II) in the range 4000–600 cm.$^{-1}$, a further confirmation of the structure suggested. Most of the peaks in the two spectra occurred in the same positions and a few varied by less than 10 cm.$^{-1}$. An extra peak was given by 5-methoxy-6-hydroxyphthalide at 1190 cm.$^{-1}$ and one by 5-hydroxy-6-methoxyphthalide at 1630 cm.$^{-1}$

Acknowledgment. We wish to pay tribute to Professor J. A. McRae, who began our work on the metameconines, and whose interest, encouragement, and help continued over a period of nearly twenty years, ending only with the completion of the present problem just before his death in April, 1960.

We wish to thank Dr. C. A. Sankey of the Ontario Paper Co., Ltd., for a generous gift of vanillin, Mrs. Thelma Eskin Habgood and G. B. Robinson for the preparation of some of the intermediates, and Miss Shelagh Courtney for the determination of the infrared spectra. The research was made possible by a grant from the National Research Council, by the grant of Fellowships to two of us (M.A. and R.Y.M.) by Canadian Industries Limited and to one of us (A.L.P.) by the Spruce Falls Power and Paper Co., Ltd.

KINGSTON, ONTARIO, CAN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

Chemistry of Aromatic Iodoso Salts. I. Reaction with Aralkyl Sulfides

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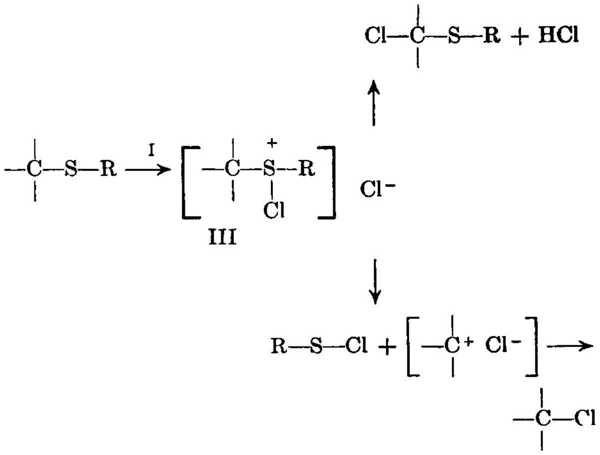
The reaction of iodobenzene dichloride (I) with dibenzyl, benzylphenyl, benzhydrylphenyl, and benzhydrylbenzyl sulfides has been investigated. The reaction proceeds with chlorination of the benzyl carbon with the first two compounds with cleavage to benzhydryl chloride and benzenesulfenyl chloride with benzhydrylphenyl sulfide and apparently by a combination of the two reaction paths in the case of benzhydryl benzyl sulfide. Reaction of iodobenzene diacetate with benzyl phenyl sulfide and dibenzyl sulfide gave the corresponding sulfoxides in 51 and 22% yield respectively.

While iodobenzene dichloride (I) has been known for over seventy years,[1] its reaction with sulfides has not been reported. It therefore appeared of interest to investigate the behavior of I with some sulfides.

The reactions of I with the sulfides studied can be summarized by the following schematic reaction path.



The formation of the chlorosulfonium chloride (III) is postulated as the first intermediate, as in the reactions of sulfides with chlorine studied by Bordwell and Pitt.[2] Decomposition of III can occur in one of two ways depending upon the nature of the organic groups attached to the sulfur atom. When one group is phenyl, benzyl, or methyl, and the other is methyl or benzyl, the intermediate reacts with the evolution of hydrogen chloride to give the α-chloro sulfide.[2] A second path by which the chlorosulfonium ion could decompose is by ionization of the intermediate to the sulfenyl halide and the carbonium ion. It should be noted here that factors that stabilize a carbonium ion greatly favor this path or reaction. It is for this

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[1] C. Willgerodt, *J. prakt. Chem.*, [2] **33**, 154 (1886).

[2] F. G. Bordwell and B. M. Pitt, *J. Am. Chem. Soc.*, **77**, 575 (1955).

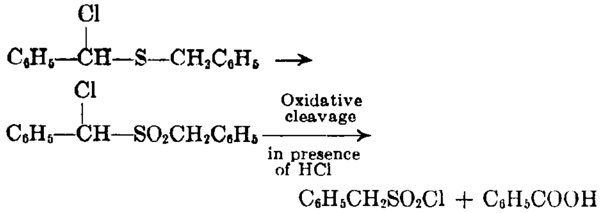
reason that one can attribute the formation of almost quantitative yields of trityl chloride[3] when one of the group is the triphenylmethyl group. The stability of the sulfenyl chloride or the nature of the group R does not seem to be a major factor when the other group is a trityl group.

Benzyl phenyl sulfide reacted with I to give a 72% yield of the α-chloro sulfide, which on hydrolysis gave benzaldehyde diphenyl mercaptal in almost quantitative yields, probably through the intermediate hemithioacetal. Oxidation of the mercaptal to the disulfone gave a product m.p. 204–205°. Laves[4] reports a melting point of 262°. The same author also claims benzaldehyde diphenyl mercaptal to be an oil. The structure of the *alpha* chloro compound was further substantiated by reaction with phenylmagnesium bromide to form benzhydryl phenyl sulfide. The reaction of I indicates a preferential attack on the carbon atom *alpha* to the sulfur. Similar observations have been made by Bordwell and Pitt[2] regarding chlorination with sulfuryl chloride reporting that reaction occurred exclusively in the side chain other than in the aromatic ring when *p*-methoxyphenyl methyl sulfide was used.

When I reacts with dibenzyl sulfide in an equimolar ratio, an oil which cannot be purified by vacuum distillation is obtained. This oil on treatment with phenylmagnesium bromide yields benzhydryl benzyl sulfide in 89% yield and on treatment with monoperphthalic acid in anhydrous ether yields α-chlorodibenzyl sulfone, indicating that the oil is mainly α-chlorodibenzyl sulfide. The infrared spectrum of the crude oil shows a strong band in the range 750–700 cm.$^{-1}$ which is characteristic of C—Cl stretching absorption in compounds containing only a single chlorine atom.[5] This characteristic band is also found in the crude oil obtained on treatment of I with benzyl phenyl sulfide and in the pure material (α-chlorobenzyl phenyl sulfide) that is obtained upon vacuum distillation of the crude oil, thus indicating that the oils obtained on treatment of dibenzyl sulfide and benzyl phenyl sulfide with I are the α-chlorosulfides where the chlorine is bonded to the α-carbon and not the sulfur atom of the sulfide molecule.

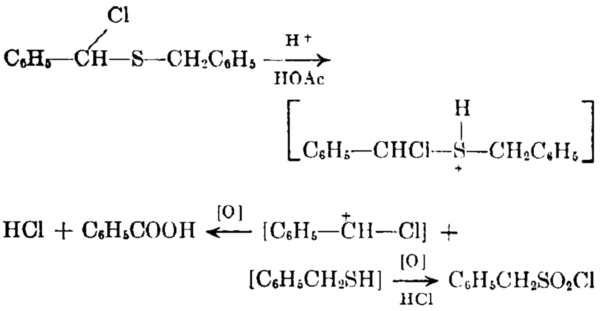
When α-chlorodibenzyl sulfide is treated with peracetic acid using glacial acetic acid as solvent, cleavage of one of the sulfur-carbon bond occurs with the formation of a 68% yield of α-phenylmethanesulfonyl chloride, benzoic acid being the only other isolable product. This reaction can be visualized to occur by one of several paths. One such sequence is outlined below as Path A, where the chlorosulfide would first be oxidized to the chlorosulfone and the chlorosulfone in the presence of hydrogen chloride would undergo oxidative cleavage to form α-phenylmethanesulfonyl chloride and benzoic acid. With this in mind α-chlorodibenzyl sulfone was dissolved in glacial acetic acid and treated with peracetic acid and hydrogen chloride gas; however, the starting chlorosulfone was recovered quantitatively. It therefore seems that cleavage of the molecule occurs prior to the oxidation of the sulfur atom to the sulfone level. A second reaction path is shown below (Path B).

PATH A



$$C_6H_5-\overset{\overset{Cl}{|}}{C}H-S-CH_2C_6H_5 \longrightarrow$$
$$C_6H_5-\overset{\overset{Cl}{|}}{C}H-SO_2CH_2C_6H_5 \xrightarrow[\text{in presence of HCl}]{\text{Oxidative cleavage}} C_6H_5CH_2SO_2Cl + C_6H_5COOH$$

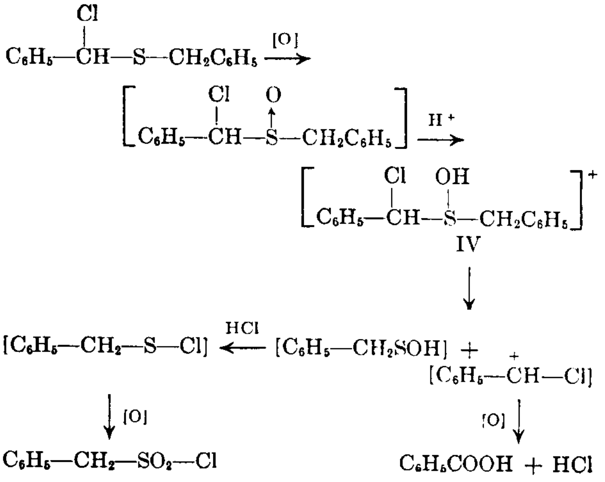
PATH B



$$C_6H_5-\overset{Cl}{C}H-S-CH_2C_6H_5 \xrightarrow[HOAc]{H^+} \left[C_6H_5-CHCl-\underset{+}{\overset{\overset{H}{|}}{S}}-CH_2C_6H_5\right]$$
$$HCl + C_6H_5COOH \xleftarrow{[O]} [C_6H_5-\overset{+}{C}H-Cl] + [C_6H_5CH_2SH] \xrightarrow[HCl]{[O]} C_6H_5CH_2SO_2Cl$$

Should it be operative, α-phenylmethanesulfonyl chloride should should be obtained on treatment of benzyl mercaptan with peracetic acid and hydrogen chloride. It was found that only a negligible amount of the sulfonyl chloride was formed. The major product of the reaction, as would be expected was α-phenylmethanesulfonic acid which was identified by conversion to the sulfonyl chloride *via* the sodium salt. It therefore seems that this reaction sequence is highly improbable. A third route is *via* a chlorosulfoxide intermediate as shown in Path C.

PATH C



$$C_6H_5-\overset{\overset{Cl}{|}}{C}H-S-CH_2C_6H_5 \xrightarrow{[O]} \left[C_6H_5-\overset{\overset{Cl}{|}}{C}H-\overset{\overset{O}{\uparrow}}{S}-CH_2C_6H_5\right] \xrightarrow{H^+} \underset{\text{IV}}{\left[C_6H_5-\overset{\overset{Cl}{|}}{C}H-\overset{\overset{OH}{|}}{S}-CH_2C_6H_5\right]^+}$$
$$\downarrow$$
$$[C_6H_5-CH_2-S-Cl] \xleftarrow{HCl} [C_6H_5-CH_2SOH] + [C_6H_5-\overset{+}{C}H-Cl]$$
$$[C_6H_5-CH_2-S-Cl] \xrightarrow{[O]} C_6H_5-CH_2-SO_2-Cl \qquad [C_6H_5-\overset{+}{C}H-Cl] \xrightarrow{[O]} C_6H_5COOH + HCl$$

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(3) K. C. Schreiber and V. Fernandez, *J. Org. Chem.*, **26**, 2478 (1961).

(4) B. Laves, *Ber.*, **25**, 355 (1892).

(5) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen and Co., Ltd., London, 1954, p. 271.

The peracid could oxidize the chlorosulfide to the chlorosulfoxide in the first step which then undergoes protonation to give the intermediate IV. It should be noted that the nature of the solvent and the acidity of the solution play an important role in this mechanism. In a solvent like glacial acetic acid the intermediate IV could easily ionize to the α-phenylmethanesulfenic acid and the chlorobenzyl carbonium ion. This type of ionization would be very difficult in a solvent like ether. Hence when α-chlorodibenzyl sulfide is treated with monoperphthalic acid in ether as solvent, oxidation occurs to give the chlorosulfone. Also the acidity of the solution is considerably lower since the phthalic acid that is formed during the reaction precipitates. It is known that 1-anthraquinone sulfenic acid, the only isolated sulfenic acid, undergoes reaction to the sulfenyl halide on treatment with hydrogen halide.[6] It is therefore conceivable that the postulated α-phenylmethanesulfenic acid intermediate could be readily converted into sulfenyl chloride which upon further oxidation would give α-phenylmethanesulfonyl chloride. Therefore, in order to show that the above mechanism was operative, several unsuccessful attempts were made to prepare the α-chlorosulfoxide. Böhme and Gran[7] have used sulfuryl chloride as a chlorinating agent for the preparation of α-chloro sulfides. Dibenzyl sulfoxide was treated with an equimolar quantity of sulfuryl chloride, however, only a 54% yield of benzaldehyde was obtained and no chlorosulfoxide. Attempted distillation of the reaction mixture under vacuum caused excessive decomposition of the α-phenylmethanesulfenyl chloride. For this reason the resulting product was oxidized with peracetic acid to isolate α-phenylmethanesulfonyl chloride and benzoic acid. It has been reported[8] that *N*-chlorosuccinimide reacts with benzyl mercaptan to form α-phenylmethanesulfenyl chloride. It was found that the addition of the chlorosuccinimide to the mercaptan gave dibenzyl disulfide whereas the reverse addition gave the α-phenylmethanesulfenyl chloride, but again it was not possible to obtain the compound in pure state by distillation due to its instability to heat. It was therefore oxidized with peracetic acid to give α-phenylmethanesulfonyl chloride as well as treated with benzyl mercaptan to give dibenzyl sulfide. It therefore seems that Path C represents a plausible reaction sequence for the formation of α-phenylmethanesulfonyl chloride upon treatment of α-chlorodibenzyl sulfide with peracetic acid or hydrogen peroxide in glacial acetic acid.

When a 2:1 molar ratio of I to dibenzyl sulfide was utilized, reaction occurred with the formation of a product, which again could not be isolated by distillation but which on hydrolysis by refluxing with water gave tetraphenylthiophene in 33.5% yield. When the crude reaction product instead of being hydrolyzed, was treated with excess of 40% peracetic acid in a solution of glacial acetic acid phenylmethanesulfonyl chloride is again obtained in 77% yield.

When benzhydryl phenyl sulfide was treated with I, cleavage of the sulfide molecule occurred giving diphenylmethyl chloride in 80% yield, the other product being presumably benzenesulfenyl chloride identified by conversion to the diphenyl disulfide upon treatment with phenyl mercaptan. As in the case of the trityl sulfides,[3] there was no evolution of hydrogen chloride gas during the course of the reaction. The formation of diphenylmethyl chloride has been further substantiated by treatment of the reaction product obtained on treatment of I with benzhydryl phenyl) sulfide (after removal iodobenzene and benzenesulfenyl chloride) with phenylmagnesium bromide to give triphenylmethane in 66% yield.

The reaction of I with benzhydryl benzyl sulfide does not seem to follow a single reaction path. This reaction is rather slow, taking about twelve hours for the complete disappearance of I at room temperature, while the reaction of I with either dibenzyl sulfide or benzyl phenyl sulfide is nearly instantaneous at room temperature. Furthermore, unlike benzhydryl phenyl sulfide there is slow evolution of hydrogen chloride gas. Treatment of the crude reaction mixture (hereafter referred to as V) with 2,4-dinitrophenylhydrazine gave a 31% yield of benzophenone 2,4-dinitrophenylhyrazone. Oxidation of V with excess of peracetic acid gave a 49% yield of α-phenylmethanesulfonyl chloride and a 70% yield of benzophenone, isolated as the 2,4-dinitrophenylhydrazone. Treatment of V with a 100% excess of phenylmagnesium bromide gave benzyl mercaptan (44%), triphenylmethane (35%), and a hydrocarbon (11%) which had an analysis corresponding to $C_{26}H_{20}$ (VI). No other products could be isolated. Monoperphthalic acid which has been used to oxidize chlorosulfides to chlorosulfones gave on reaction with V a 51% yield of α-phenylmethanesulfonyl chloride and a 35% yield of benzophenone and none of the expected α-chlorobenzhydryl benzyl sulfone. V reacted with benzyl mercaptan with evolution of hydrogen chloride gas and the formation of dibenzyl disulfide. Vacuum distillation of V gave a fraction, b.p. 115–125°/0.2., mm., which gave benzhydryl benzyl sulfide (49%) and benzhydryl phenyl sulfide (54%) upon treatment with a glacial acetic acid solution of benzyl mercaptan and phenyl mercaptan respectively. From these last reactions it seems evident that this fraction contains about 50% of diphenylmethyl chloride. It would therefore be inferred that at least 50% of the chlorosulfonium chloride

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[6] N. Kharasch, S. J. Potempa, and H. L. Wehrmeister, *Chem. Revs.*, **39**, 288 (1946).

[7] H. Böhme and H. S. Gran, *Ann.*, **581**, 136 (1953).

[8] H. Emde, Ger. Patent **804,572** (1951); *Chem. Abstr.*, **46**, 530 (1952).

intermediate decomposes giving the sulfenyl chloride and diphenylmethyl chloride.

The formation of benzyl mercaptan in the Grignard reaction is rather surprising because benzenesulfenyl chloride has been reported[9] to react with phenylmagnesium bromide to give diphenyl sulfide. While it would be expected that α-chlorobenzhydryl benzyl sulfide reacts with phenylmagnesium bromide to yield benzyl trityl sulfide just as α-chlorodibenzyl sulfide or α-chlorobenzyl phenyl sulfide gives benzhydryl benzyl sulfide and benzhydryl phenyl sulfide respectively, the greater steric crowding in the α-chlorobenzhydryl benzyl sulfide may give rise to another type of reaction in which a cleavage of the carbon sulfur bond occurs to yield trityl chloride and the bromomagnesium salt of benzyl mercaptan. This would account for the formation of benzyl mercaptan and of the hydrocarbon VI, since it has been reported that triphenylmethyl chloride reacts with phenylmagnesium bromide to give a mixture of several hydrocarbons.[10]

As already mentioned V reacts with 2,4-dinitrophenylhydrazine to give the 2,4-dinitrophenylhydrazone of benzophenone in 31% yield. Diphenylmethyl chloride does not react with this reagent to give a hydrazone. Neither does diphenylmethyl chloride react with I, so that if any benzophenone dichloride formed, it is not due to reaction of diphenylmethyl chloride with I. It therefore seems that simple cleavage of the initially formed chlorosulfonium intermediate is not the only pathway of the reaction. On the basis of the reaction of dibenzyl sulfide and phenyl benzyl sulfide, another likely product of the reaction might be α-chlorobenzhydryl benzyl sulfide. This being a derivative of benzophenone, it would be expected to react with 2,4-dinitrophenylhydrazine to give the hydrazone. This path would also account for the evolution of hydrogen chloride during the reaction of I with benzhydryl benzyl sulfide.

Judging from the analysis of the fraction b.p. 115/25°/0.2 mm. obtained on vacuum distillation of V it is most likely a chemical evidence mentioned above already indicates the presence of benzhydryl chloride mixture containing 90% benzhydryl chloride and 10% benzylsulfenyl chloride calculates as follows: (C, 74.66; H, 5.32; S, 2.01; Cl, 18.07) which is in good agreement with the found values of C, 74.64; H, 5.37; S, 2.02; Cl, 18.17. Further work to elucidate this reaction is being conducted.

Reaction of benzyl phenyl sulfide and dibenzyl sulfide with iodobenzene diacetate gave, as expected from the result of Szmant and Suld[11] the corresponding sulfoxides, however, the yields were not very good.

EXPERIMENTAL[12]

Iodobenzene dichloride (I) was prepared by the method of Lucas and Kennedy.[13]

Iodobenzene diacetate was prepared by the method of Pausacker.[14]

TABLE I

Sulfide	M.P. Found	M.P. Lit.	Ref. for Prepn.
Benzyl phenyl	40–41	40–41[a]	[a]
Benzhydryl benzyl	70–71	70.5[b]	[c]
Benzhydryl phenyl	78–79	78[d]	[d]
Dibenzyl	49–50	49[d]	[d]

[a] R. Pummerer, *Ber.*, **43**, 1406 (1910). [b] A. Schönberg, O. Schütz, and J. Peter, *Ber.*, **62B**, 1668 (1929). [c] Made by adapting the method of Finzi and Bellavita. [d] C. Finzi and V. Bellavita, *Gazz. chim. ital.*, **62**, 699 (1932).

Reactions of iodobenzene dichloride (I). *With benzyl phenyl sulfide* (A). To a flask with calcium chloride drying tube containing 19.5 g. (0.097 mole) of benzyl phenyl sulfide in 100 ml. of dry chloroform, were added 26.5 g. (0.096 mole) of I in small quantities with constant shaking. During the addition there was copious evolution of hydrogen chloride gas. The mixture was set aside for about an hour. After removal of the solvent the mixture was distilled *in vacuo*. Two fractions were collected; the first was iodobenzene distilling at 48–50°/2 mm., while the second fraction boiling at 149°/2 mm. was identified to be α-chlorobenzyl phenyl sulfide[2] (10.4 g.); yield 72.2%. Treatment of the chlorosulfide with a 100% excess of phenylmagnesium bromide followed by hydrolysis with ice-water mixture yielded benzhydryl phenyl sulfide; m.p. and mixed m.p. with authentic sample 78–79°. Oxidation of the benzhydryl phenyl sulfide to the sulfone with 30% hydrogen peroxide in glacial acetic acid gave product melting at 187–188°, lit.[15] m.p. 188°.

(B). The procedure in this experiment was similar to that in (A) except that, instead of isolating the α-chloro compound, the mixture was hydrolyzed by refluxing for 3 hr. with 200 ml. of water. The organic layer was separated and the aqueous layer was repeatedly extracted with 50-ml. portions of chloroform. The organic layers were combined, washed with water, dried over Drierite, and distilled *in vacuo* after removal of the solvent. Iobobenzene and benzaldehyde distilled over at 55–56°/5 mm. The benzaldehyde (53%) was isolated as the 2,4-dinitrophenylhydrazone. The distillation residue solidified in the ice box, m.p. 49–50°, and was identified as benzaldehyde diphenyl mercaptal (yield based on sulfur 90%). Mixed melting point with authentic sample prepared according to Hauptmann and Wladislaw[16] gave no depression. Oxidation of benzaldehyde diphenyl mercaptal with excess of 40% peracetic acid to the disulfone gave product m.p. 204–205°, lit[4] m.p. 262°.

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(9) E. Emmet Reid, *Organic Chemistry of Bivalent Sulfur*, Chemical Publishing Company, New York, 1959, Vol. I, p. 275.

(10) M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice Hall Inc., New York, N. Y., 1954, p. 1051.

(11) H. H. Szmant and G. Suld, *J. Am. Chem. Soc.*, **78**, 3400 (1956).

(12) All melting points and boiling points are uncorrected. Analyses were performed by A. Bernhardt; Galbraith Microanalytical Labs or Elek Microanalytical Labs.

(13) H. J. Lucas and E. R. Kennedy, *Org. Syntheses*, **Coll. Vol. III**, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 482.

(14) K. H. Pausacker, *J. Chem. Soc.*, 107 (1953).

(15) R. Knoll, *J. prakt. Chem.*, (2) **133**, 42 (1926).

(16) H. Hauptmann and B. Wladislaw, *J. Am. Chem. Soc.*, **72**, 707 (1950).

Anal. Calcd. for $C_{19}H_{16}O_4S_2$: C, 61.27; H, 4.33; S, 17.22. Found: C, 61.54; H, 4.41; S, 17.42.

With dibenzyl sulfide (A). To 21.5 g. (0.1 mole) of dibenzyl sulfide in 100 ml. of dry chloroform I (27.5 g, 0.1 mole) was added. Vigorous reaction ensued with the evolution of hydrogen chloride gas. After standing overnight, the chloroform and iodobenzene were removed by distillation *in vacuo.* Attempts to isolate the chloro compound by distillation failed due to decomposition. Thus, the crude residue was treated with a 100% excess of phenylmagnesium bromide followed by hydrolysis with ice water mixture to give 25.8 g. (88.8%) of crude benzhydryl benzyl sulfide, m.p. 70–71°, which gave no depression with authentic sample. Oxidation of benzhydryl benzyl sulfide with 30% hydrogen peroxide in glacial acetice acid gave the sulfone, m.p. 153–154°.

Anal. Calcd. for $C_{20}H_{18}O_2S$: C, 74.50; H, 5.63; S, 9.92. Found: C, 74.74; H, 5.55; S, 9.72.

(B) To a solution of 17.8 g. (0.083 mole) of dibenzyl sulfide dissolved in 50 ml. of dry chloroform, 45.8 g. (0.167 mole) of I were added in small quantities with swirling. After standing overnight the chloroform was distilled, and the residue refluxed with 50 ml. of water 1.5 hr. The mixture was extracted with ether and the ether solution was shaken with three 50-ml. portions of sodium bisulfite solution. Decomposition of the bisulfite addition compound with hydrochloric acid yielded 1.6 g. of benzaldehyde, identified as the 2,4-dinitrophenylhydrazone. The ether layer was washed with two 10-ml. portions of water, dried over Drierite, the ether distilled, and the iodobenzene removed by vacuum distillation. The residue was chromatographed using an alumina column and petroleum ether (b.p. 30–60°) followed by benzene as eluents, fractions were collected yielding from the first two fractions a solid, sublimation of which under reduced pressure (21 mm.) gave 0.8 g. of stilbene, m.p. 124–125°. The residue from sublimination was identified as tetraphenyl thiophene (5.4 g., 33.5%). Recrystallization from benzene-ethanol mixture gave needles, m.p. 183–184°, lit.[17] m.p. 183–184°, showing no depression with a sample prepared according to Baumann and Klett.[17] Ultraviolet and infrared spectra of the reaction product was identical to that of the authentic sample.

(C). To a solution of 21.4 g. (0.1 mole) of dibenzyl sulfide in 100 ml. of anhydrous chloroform 27.5 g. (0.1 mole) of I was added in small quantities with shaking. The mixture was kept overnight stoppered with the drying tube. After distillation of the chloroform and iodobenzene under reduced pressure, the mixture was dissolved in 100 ml. of glacial acetic acic and 50 ml. of 40% peracetic acid added gradually with shaking. After 12 hr. at room temperature, the mixture was poured into a beaker containing crushed ice. The solid that separated was filtered and crystallized from a mixture of benzene and petroleum ether to give 13.0 g. (68.2%) of α-phenylmethanesulfonyl chloride m.p. 81–83°, which after repeated crystallization from benzene and petroleum ether gave needles, m.p. and mixed m.p. 92–93°, lit.[18] m.p. 91–92°.

(D). The α-chlorodibenzyl sulfide was prepared according to the method of Böhme and Gran,[7] and oxidized as above with peracetic acid to given an 84% yield of α-phenylmethanesulfonyl chloride, m.p. 92–93°. Treatment of the reaction product with ammonia gave α-phenylmethanesulfonylamide, m.p. 103–4°, which gave no depression with authentic material.[19] From the aqueous portions, after separation of the sulfonyl chloride, a 35% yield of benzoic acid was obtained after distilling the water and acetic acid under reduced pressure and extraction of the residue with sodium, hydroxide, and acidification with dilute hydrochloric acid. A negative test with 2,4-dinitrophenylhydrazine reagent was obtained on the remaining liquid.

With benzhydryl phenyl sulfide (A). To a solution of 22.5 g. (0.1 mole) of benzhydryl phenyl sulfide in 300 ml. of dry carbon tetrachloride 27.5 g (0.1 mole) of I was added in small quantities with constant swirling and allowed to stand at room temperature overnight. There was no evolution of hydrogen chloride gas. The carbon tetrachloride was removed and the residue distilled in vacuo. Three fractions were collected: (i) 18.1 g. of liquid, b.p. 45–58°/4.5 mm. which contained mainly iodobenzene, but also contained phenyl sulfenyl chloride as determined by conversion to diphenyl disulfide with phenyl mercaptan. From the diphenyl disulfide isolated it was calculated that fraction i contained 4.3 g. (0.03 mole; 38%) of phenyl sulfenyl chloride; (ii) 5.7 g. of liquid, b.p. 80–82°/1 mm., which when treated with phenyl mercaptan reacted with the evolution of hydrogen chloride to yield 4.8 g. of diphenyl disulfide representing 3.2 g. (0.02 mole; 28%) of phenyl sulfenyl chloride in fraction ii; and (iii) 12.6 g. (0.062 mole; 77.5%) of diphenylmethyl chloride, b.p. 135–138°/4 mm., lit.[20] b.p. 158.5–159.5°/12 mm. Hydrolysis of fraction iii with 10% aqueous sodium hydroxide gave benzhydrol, m.p. 68–69°, lit.[21] m.p. 68°, that did not depress the melting point of an authentic sample.

(B). To a solution of 9.4 g. (0.034 mole) of benzhydryl phenyl sulfide in 100 ml. of chloroform was added 9.4 g. (0.034 mole) of I in small quantities with constant shaking. After the mixture stood for 24 hr. at room temperature, the solvent and iodobenzene were removed and the residue treated with phenylmagnesium bromide, prepared from 2 g. of magnesium and 13 g. of bromobenzene. The mixture was stirred for 12 hr. and then hydrolyzed with a saturated ammonium chloride solution and extracted with ether. The ether extracts were dried over Drierite, filtered, and the solvent distilled, yielding 5.5 g. (66%) of triphenylmethane, m.p. and mixed m.p., 90–91°, lit.[22] m.p. 90°.

With benzhydryl benzyl sulfide. (A). To a solution of 11.6 g. (0.04 mole) of benzhydryl benzyl sulfide in 100 ml. of dry carbon tetrachloride was added 11.0 g (0.04 mole) of I in small quantities. There was slow evolution of hydrogen chloride gas. The mixture was allowed to stand overnight at which time all of I had disappeared. The mixture was treated with 100 ml. of 40% peracetic acid in small quantities with cooling. After the addition of the peracid was complete, the reaction mixture was stirred for 12 hr., the acetic acid and carbon tetrachloride were evaporated under reduced pressure, yielding a heavy viscous oil (18 g.) (i). Part of this oil (1.9 g.) was extracted with several 10 to 15 ml. portions of petroleum ether (b.p. 30–60°) and from the extracts was obtained α-phenylmethane sulfonyl chloride (0.4 g., 49%), m.p. 92–93°, which did not depress the melting point of an authentic sample. (ii). Six grams of the viscous oil was treated with 2,4-dinitrophenylhydrazine reagent to obtain 3.4 g. (70.5%) of benzophenone phenylhydrazone, m.p. and mixed m.p. 240–241°. (B). To a solution of 29 g. (0.1 mole) of benzhydryl benzyl sulfide in 160 ml. of dry carbon tetrachloride was added 27.5 g. (0.1 mole) of I and the mixture allowed to stand overnight. Total volume at this stage was 188 ml. (i). To 25 ml. of this mixture was slowly added with stirring 30 ml. of monoperphthalic acid in ether. The phthalic acid which separated was filtered and the solvent evaporated from the filtrate to give a viscous oil which was extracted several times with petroleum ether (b.p. 30–60°) to give 1.3 g. 51%) of α-phenylmethane sulfonyl chloride, m.p. and mixed m.p. 92–93°, upon evaporation of the petroleum ether. The mother liquor from the petroleum ether extraction was treated with 2,4-dinitrophenylhydrazine reagent to give 1.7 g. (35%) of benzophenone phenylhydrazone. (ii). To another 25 ml. of the original solution was added 1.7 g benzyl mercaptan with cooling. The solution which was originally yellow turned colorless with copious evolution of

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[19] T. B. Johnson and J. A. Ambler, *J. Am. Chem. Soc.*, **36**, 381 (1914).

[20] A. M. Ward, *J. Chem. Soc.*, 2288 (1927).

[21] C. S. Marvel and N. A. Hansen, *Org. Syntheses*, **Coll. Vol. I,** 2nd ed., 1956, p. 91.

[22] J. F. Norris, *Org. Syntheses*, **Coll. Vol. I,** 548 (1941).

hydrogen chloride gas. Evaporation of the solvent gave 2.7 g. (82.4%) of dibenzyl disulfide, m.p. 71–72°, lit.[23] m.p. 69–70°. that did not depress the melting point of an authentic sample. (iii). Eighty-eight milliliters of the original mixture was stripped of the solvent and distilled under vacuum to give two fractions: (a), 7.5 g. of liquid b.p. 40–45°/0.2 mm. which contains chiefly iodobenzene and (b). 10.3 g. of liquid b.p. 115–25°/0.2 mm. Distillation was discontinued due to decomposition of the liquid in the pot.

Anal. Fraction (b). Found: C, 74.64; H, 5.37; Cl, 18.17; S, 2.02.

Three and three-tenth grams of fraction (b) was dissolved in 25 ml. of glacial acetic acid and treated with 1.0 g. of benzyl mercaptan. After 2 days, 2.1 g. of crystals, m.p. 70–71° had separated. Mixed melting point of this compound with benzhydryl benzyl sulfide gave no depression; yield 48.6%.

Two and two-tenth grams of fraction (b) was dissolved in 25 ml. of glacial acetic acid and treated with 0.7 g. of phenyl mercaptan. The mixture was allowed to stand for 2 days and the solvent removed under reduced pressure to give 1.5 g. of solid m.p. 78–79°, from ethanol. Mixed melting point with benzhydryl phenyl sulfide did not depress the melting point; yield 54%.

(iv). Twenty-five milliliters of the original mixture, after removal of the solvent, was treated with 2,4-dinitrophenylhydrazine reagent to give 1.5 g. of hydrazone that did not lower the melting point of benzophenone 2,4-dinitrophenylhydrazone, m.p. 240–241°; yield 31%.

(C). To a solution of 14.5 g. (0.05 mole) of benzhydryl benzyl sulfide in 200 ml. of carbon tetrachloride in a flask provided with a calcium chloride tube was added 13.8 g (0.05 mole) of I in the usual manner. The mixture was allowed to stand overnight, the carbon tetrachloride distilled and the iodobenzene removed by distillation *in vacuo*, dissolved in about 100 ml. of anhydrous ether and slowly added to a well stirred solution of phenylmagnesium bromide, prepared from 3.6 g. of magnesium and 23.6 g. of bromobenzene in 200 ml. of ether. After the addition was complete, the mixture was allowed to stir for 12 hr. and then hydrolyzed with 60 ml. of a saturated solution of ammonium chloride. The ether layer was separated from the aqueous layer and the latter extracted several times with small quantities of ether. The combined ether extracts were dried over Drierite and then distilled to remove solvent. Distillation under vacuum gave 2.7 g. (44%) of benzyl mercaptan b.p. 65–70°/0.05 mm., confirmed by oxidation with iodine to dibenzyl disulfide, m.p.[23] 71–72°. Continuation of the distillation yielded 2.7 g. of biphenyl, m.p. 68–69°. Further distillation was impossible because of excessive decomposition. Hence the sticky semisolid residue in the pot was cooled in an ice box to obtain 1.4 g. of solid, m.p.[22] 91–92°, recrystallized from ethanol, that did not lower the melting point of an authentic sample of triphenylmethane. An aliquot (1.5 g. of the total residue of 10.7 g.) was chromatographed through an alumina column and eluted successively with petroleum ether, carbon tetrachloride, ethyl acetate, and methanol to obtain 0.4 g. of triphenylmethane from the petroleum ether fraction. Only a viscous mass could be obtained from the carbon tetrachloride solution, the ethyl acetate or methanol fractions yielding no product; total yield of triphenylmethane, 34.8%.

In another reaction 4 g. of benzhydryl benzyl sulfide was treated with I in the usual manner and the reaction mixture after the removal of the solvent and iodobenzene was treated with 0.05 mole of phenylmagnesium bromide and the mixture was stirred overnight. Hydrolysis with dilute hydrochloric acid, followed by extraction with ether yielded 0.4 g. (11%) of solid m.p. 200–204°.

Anal. Calcd. for $C_{25}H_{20}$: C, 93.71; H, 6.29. Found: C, 93.92; H, 5.82.

Reaction of sulfuryl chloride with dibenzyl sulfoxide. To an ice cooled solution of 11.5 g. (0.05 mole) of dibenzyl sulfoxide (m.p. 132–133°) in 300 ml. of dry carbon tetrachloride was slowly added 6.8 g. (0.05 mole) of sulfuryl chloride in 100 ml. of the same solvent with constant stirring over a period of 1 hr. After the addition of sulfuryl chloride was completed, the mixture was stirred for an additional half hour during which there was copious evolution of hydrogen chloride. Thirty milliliters of 40% peracetic acid was next added dropwise and the mixture was stirred overnight. Evaporation of the solvent under vacuum gave a white solid which was recrystallized from a mixture of benzene and petroleum ether to give 6.5 g. (68.2%) of α-phenylmethanesulfonyl chloride, m.p.[18] 92–93°. From the mother liquor was obtained 1.9 g. (31.1%) of benzoic acid.

In a separate experiment the reaction product obtained on treatment of sulfuryl chloride with benzyl sulfoxide was distilled under vacuum in order to isolate the primary reaction product. Excessive decomposition occurred with only a few drops of purple colored liquid distilling. A 54% yield of benzaldehyde was obtained as the 2,4-dinitrophenylhydrazone derivative which was prepared by treating a small quantity of the reaction mixture with 2,4-dinitrophenylhydrazine before distillation.

Attempted preparation of α-phenylmethanesulfenyl chloride. A. To a solution of 11.4 g. (0.092 mole) of benzyl mercaptan in 200 ml. of dry carbon tetrachloride was added 13.3 g. (0.1 mole) of *N*-chlorosuccinimide in small quantities with cooling. The reaction mixture was allowed to stand overnight when the succinimide that had precipitated was filtered and the filtrate stripped of the solvent under vacuum. The solid mass that was left was crystallized from ethanol to give 6.5 g. (57.5%) of dibenzyl disulfide m.p.[23] 71–73, which did not depress the melting point of an authentic sample.

(B). To ice-cooled solution of 7 g. (0.052 mole) of *N*-chlorosuccinimide in 300 ml. of dry carbon tetrachloride was added drop-wise 6.2 g. (0.05 mole) of benzyl mercaptan in 100 ml. of carbon tetrachloride in a dry atmosphere with continuous stirring. On completion of the addition, the mixture was stirred for an additional hour, and 25 ml. of 40% peracetic acid was then added slowly. The mixture was stirred overnight, it was then stripped of the solvent under vacuum and extracted with benzene. The succinimide that was formed during the reaction remained undissolved. Crystallization of the α-phenylmethansulfonyl chloride from the benzene solution with petroleum ether gave 7.4 g. of product, m.p.[18] 92–93°.; yield 77.6%.

Reactions of iodobenzene diacetate (II). *With benzyl phenyl sulfide.* Benzyl phenyl sulfide (2.0 g., 0.01 mole) was added to a solution of 3.2 g. (0.01 mole) of II in 50 ml. of dry benzene and the mixture was allowed to stand for 2 days. Concentration of the mixture yielded an oil which crystallized to give 0.8 g. of a compound m.p. 124–125° after one recrystallization from benzene and petroleum ether. Further concentration yielded 0.3 g. of the compound. Mixed m.p. with pure benzyl phenyl sulfoxide[24] gave no depression; yield 51%.

With dibenzyl sulfide. The reaction was performed in a similar way to that described for the benzyl phenyl sulfide using 0.01 mole of the sulfide and II; 0.5 g. of the sulfoxide, m.p. 133–134°, was obtained[24]; yield 22%.

Preparation of α-chlorodibenzyl sulfone. Three grams (0.01 mole) of the crude oil obtained by the reaction of an equimolar quantity of benzyl sulfide and sulfuryl chloride was dissolved in about 100 ml. of anhydrous ether and 60 ml. of an ethereal solution of monoperphthalic acid prepared according to the method of Stahmann and Bergmann[25] was added slowly with cooling. The mixture was set aside for 48 hr. and the phthalic acid which precipitated was filtered, the filtrate evaporated to dryness, and the solid mass

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[23] E. Fromm and P. Schmoldt, *Ber.*, **40**, 2870 (1907).

[24] R. L. Shriner, H. C. Struck, and W. J. Jorison, *J. Am. Chem. Soc.*, **52**, 2066 (1930).

[25] M. A. Stahmann and M. Bergmann, *J. Org. Chem.*, **11**, 589 (1946).

extracted with dry benzene from which 1.4 g. of white crystals could be obtained, m.p. 118–19°, lit. m.p. 122; yield 52.3%.

Reaction of α-chlorodibenzyl sulfone with peracetic acid. A. To a solution of 0.5 g. of α-chlorodibenzyl sulfone in 15 ml. of glacial acetic acid was added 1 ml. of 40% peracetic acid. After letting the reaction mixture stand at room temperature for 24 hr., it was poured into 25 g. of crushed ice and filtered to recover a quantitative amount of the chlorosulfone that did not depress the melting point of pure starting material.

B. The above experiment was repeated using exactly the same quantities and the reaction mixture was saturated with hydrogen chloride gas and allowed to stand for 24 hr. at room temperature. In this case also a quantitative yield of the starting material was recovered by using the above procedure for isolation.

Reaction of benzyl mercaptan with peracetic acid. To 5.6 g. of benzyl mercaptan (0.045 mole) in 100 ml. of glacial acetic acid was slowly added 25 ml. of 40% peracetic acid with cooling and constant shaking. The mixture was saturated with hydrogen chloride gas for a period of 10 min. and set aside for 24 hr. Upon pouring the mixture into crushed ice 0.3 g. of solid was obtained which did not depress the melting point of an authentic sample of α-phenylmethanesulfonyl chloride, m.p. 92–93°. Evaporation of the aqueous solution in vacuum gave a deliquescent solid which was treated with a solution of 2 g. of sodium hydroxide in 10 ml. of water to obtain 7.5 g. of crystals upon evaporation. Treatment of 5 g. of this compound with 5.4 g. of phosphorus pentachloride in phosphorus oxychloride according to Johnson and Ambler[10] gave 2.8 g. of α-phenylmethanesulfonyl chloride.

Reaction of I with benzyl phenyl sulfone. To a solution of 19.5 g. (0.084 mole) of benzyl phenyl sulfone in 100 ml. of dry chloroform in a flask provided with a calcium chloride tube was added 23 g. (0.084 mole) of I. No reaction seemed to have occurred even after the mixture was allowed to stand for a week. It was then filtered to remove unchanged I and from the filtrate 18.2 g. of benzyl phenyl sulfone (m.p. 145–46°) was recovered.

Reaction of I with diphenylmethyl chloride. To a solution of 5 g. (0.025 mole) of diphenylmethyl chloride in 50 ml. of carbon tetrachloride was added 6.8 g. of I. No apparent reaction occurred. The mixture was allowed to stand at room temperature for 8 days. The unchanged I was filtered (4.0 g.) and the filtrate distilled in vacuum to give 1.2 g. of iodobenzene b.p. 40–45°/0.05 mm. and 4.6 g. of unchanged diphenylmethyl chloride b.p. 110–15°/0.05 mm. The recovered diphenylmethyl chloride did not give a precipitate with 2,4-dinitrophenylhydrazine.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HOPE COLLEGE]

A Study of the Condensation of Thianaphthene with Formaldehyde

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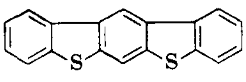
The condensation of thianaphthene with formaldehyde is promoted by hydrogen chloride, aluminum chloride and boron trifluoride catalysts. Evidence is presented that the products obtained consist of di(3-thianaphthenyl)methane (II) and 2,3-di(3-thianaphthenylmethyl)thianaphthene (III) besides higher molecular weight compounds of unknown structure. The ratio in which the above compounds are formed varies with the catalyst used as well as with the reaction time. Compound II was also prepared by the reaction of 3-chloromethylthianaphthene and 3-thianaphthenylmagnesium bromide. The infrared spectrum and the melting point of the dibromide derivative were identical with those of the thianaphthene-formaldehyde condensation product. The isomeric compound, 3-(2-thianaphthenylmethyl)thianaphthene (IV) was prepared and its properties compared with those of II.

This reaction seemed of interest since the expected methylene compounds were unknown and it was hoped that the greater reactivities of the 2- and 3- positions over positions in the benzene nucleus would increase the tendency toward the formation of relatively simple compounds. It was thought possible that compounds such as the following (I) might be obtained since the aluminum chloride catalyzed condensation of benzene and formaldehyde yields large amounts of anthracene as well as diphenylmethane.[1] Also it was of interest to obtain some accurate information about the isomer distribution in these reactions since few careful studies of electrophilic substitution involving thinaphthene have been undertaken. The reported study was undertaken to determine the conditions necessary for and the nature of the products from the reaction between thianaphthene and formaldehyde.

The results using hydrogen chloride, aluminum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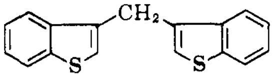
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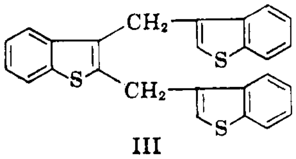
III

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