THIOCARBONYLS. IV. THE STRUCTURE OF DIFLUORYL TRISULFIDE AND DIBENZOPHENONE TRISULFIDE[1]

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When thiobenzophenone was exposed to the action of dry air for a long time it was partially converted to a trisulfide having the formula $C_{26}H_{20}S_3$ (1, 2). When this trisulfide was heated above its melting point, it was quantitatively converted to thiobenzophenone and sulfur. Two possible structures, I and II, were suggested for this compound.
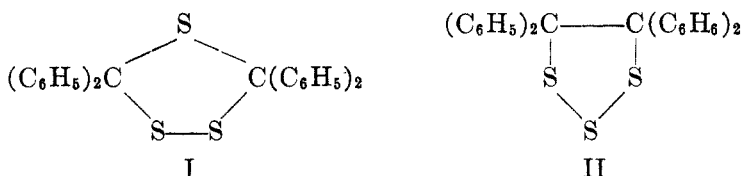
Structure I is most probable, since a compound of structure II would be likely to form tetraphenylethylene rather than thiobenzophenone on heating. A third possible structure, III, containing the dative sulfur atom, might also be considered.
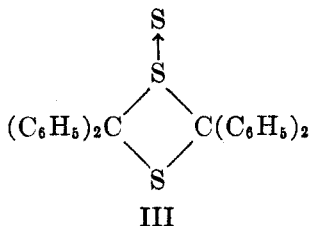
Thiofluorenone also yielded a yellow trisulfide of unknown structure, having the formula $C_{26}H_{16}S_3$, after long exposure to air (3).

These two compounds are probably members of the same series, the important characteristic of which is the arrangement of the sulfur atoms, illustrated in formulas I, II, and III. Formula III was readily eliminated on the basis of two simple reactions. Neither the dibenzophenone trisulfide nor the difluoryl trisulfide showed any labile sulfur by the lead acetate test (4), a characteristic of the dative sulfur bond. Both compounds were soluble in hot concentrated al-

kali, but insoluble in cold alkali, indicating the presence of a disulfide link (5) which is found in either I or II, but not in III. Furthermore, parachor and viscosity measurements on trisulfides and polysulfides indicate that the dative sulfur atom is not found in compounds having less than three sulfur atoms in a linear arrangement (6).

It was therefore necessary to devise experiments which would distinguish between structures A and B.

A   B
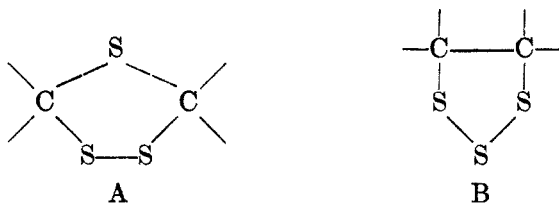
Recently Lee and Dougherty (7) oxidized methylene disulfides to sulfonyl chlorides and formaldehyde. A study of the possible equations for the reaction of chlorine and water on the trisulfide showed that a quantitative estimate of the products of the reaction would indicate the structure of the sulfur-carbon ring. Thus, if structure A is the correct one, the reaction may be written in three possible ways. (Equations 1, 2, and 3).

1. $+ 9Cl_2 + 9H_2O \longrightarrow$

$$\diagdown C(SO_2Cl)_2 + \diagdown C{=}O + H_2SO_4 + 16HCl$$

2. $+ 10Cl_2 + 11H_2O \longrightarrow$

$$\diagdown C(SO_2Cl)Cl + \diagdown C{=}O + 2H_2SO_4 + 18HCl$$

3. $+ 11Cl_2 + 12H_2O \longrightarrow$

$$2 \diagdown C(Cl)_2 + 3H_2SO_4 + 18HCl$$
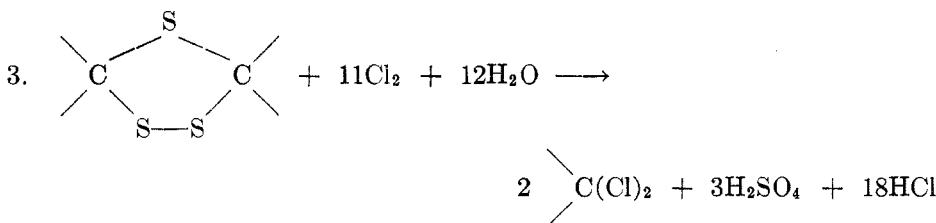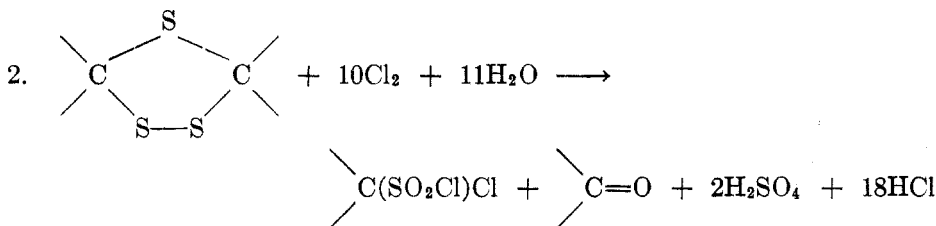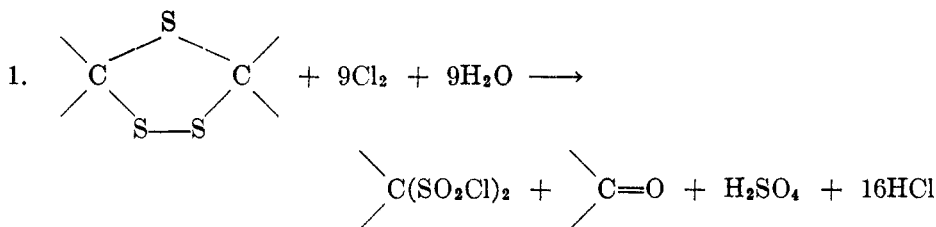
The path of the reaction in this case may be determined by isolation of the disulfonyl chloride, chlorosulfonyl chloride, or ketodichloride, as the case may be, and by determination of the molar ratio of sulfuric acid produced.

If, however, the compound has ring structure B, one mole each of disulfonyl chloride and sulfuric acid should be formed for each mole of trisulfide oxidized, as in equation 4.

$$4. \quad \underset{\underset{S-S-S}{|}}{\overset{|}{-C}}-\underset{\overset{|}{}}{\overset{|}{C}}- \; 8Cl_2 \; + \; 8H_2O \; \rightarrow \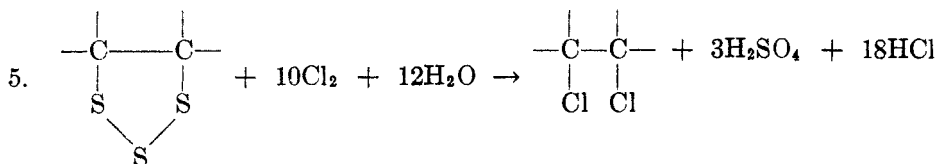; \underset{\underset{SO_2Cl}{|}}{\overset{|}{-C}}-\underset{\underset{SO_2Cl}{|}}{\overset{|}{C}} \quad + \; H_2SO_4 \; + \; 14HCl$$
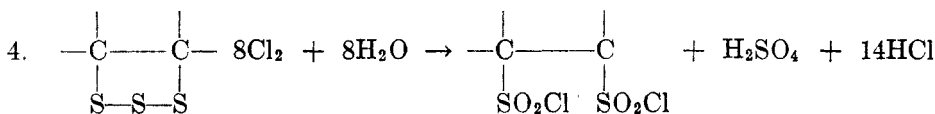
Since ethane-1,2-disulfonyl chlorides are somewhat unstable, readily losing sulfur dioxide (8), and benzylsulfonyl chlorides also lose sulfur dioxide at slightly elevated temperatures (9), it would seem possible that a 1,2-disulfonyl chloride having phenyl or bis-diphenylene groups attached to the two carbon atoms would lose sulfur dioxide to give a dichloride. The liberated sulfur dioxide would be oxidized to sulfuric acid by free chlorine. Therefore structure B might yield an ethane-1,2-dichloride, as in equation 5.

$$5. \quad \underset{\underset{S}{\overset{|}{\underset{\diagdown}{}}}\;\;\underset{S}{\overset{|}{\underset{\diagup}{}}}}{\overset{|}{-C}-\overset{|}{C}-} \quad + \; 10Cl_2 \; + \; 12H_2O \; \rightarrow \; \underset{\underset{Cl}{|}\;\underset{Cl}{|}}{\overset{|}{-C}-\overset{|}{C}-} \; + \; 3H_2SO_4 \; + \; 18HCl$$
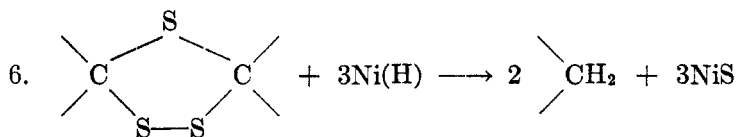
When the dibenzophenone trisulfide was treated with chlorine gas and water in cold glacial acetic acid for two hours, 1.96 moles of benzophenone dichloride per mole of trisulfide was isolated and identified by conversion to benzophenone by hydrolysis. In addition, 2.94 moles of sulfuric acid, determined as barium sulfate, was isolated per mole of trisulfide.

The treatment of the difluoryl trisulfide with chlorine gas and water likewise yielded 2.91 moles of sulfate per mole of trisulfide; however, the fluorene moiety was chlorinated during the reaction and 1.98 moles of an x,9,9-trichlorinated fluorene per mole of trisulfide was isolated. This trichlorinated product yielded a chlorofluorenone on hydrolysis, showing that approximately two moles of keto-dichloride was formed per mole of trisulfide in this reaction also.

The data are in accordance with the structure represented by A and with equation 3. However, Gomberg and Bachmann (10) have shown that the carbon-to-carbon bond of benzpinacol is cleaved by halogens or oxygen. Therefore, it would be possible for the carbon-to-carbon bond in the ethane-1,2-disulfonyl chloride which would be obtained from structure B (equation 4) to be cleaved similarly under the conditions of the reaction, to yield the keto-dichlorides actually obtained.

Recently Mozingo, Wolf, Harris, and Folkers (11) described the preparation of Raney nickel containing a large amount of adsorbed hydrogen which is useful in the reductive desulfurization of sulfur compounds. However, under certain conditions nickel has been found to cause coupling with sulfur compounds of the thiocarbonyl type (12, 13). In order to test the usefulness of this reagent on compounds of the type under investigation, dithiofluorenone (IV) was refluxed in an alcohol-benzene mixture with the nickel preparation, and 82% of the theo-

retical amount of fluorene (V) was obtained. The results of this experiment indicated that this reaction would be applicable to compounds having structure A or B. If the structure of the trisulfides was represented by A, the product of the reaction with Raney nickel would be diphenylmethane or fluorene (equation 6).

However, if B represents the correct structure, then tetraphenylethane or bis-diphenyleneethane should be produced (equation 7).
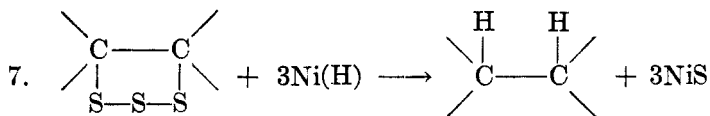

Treatment of the dibenzophenone trisulfide with the nickel preparation gave an 85% conversion to diphenylmethane, which was isolated and identified by physical constants and oxidation to benzophenone. The difluoryl trisulfide was converted by similar treatment to fluorene in rather low yield.

On the basis of these oxidation and reduction studies, the trisulfides formed when thiobenzophenone and thiofluorenone are exposed to the action of dry air are respectively 3,3,5,5-tetraphenyldimethylene-1,2,4-trisulfide, (I), and 3,5-bis-diphenylenedimethylene-1,2,4-trisulfide (VII).

The x,9,9-trichlorofluorene, that was isolated from the reaction of chlorine gas and water on 3,5-bis-diphenylenedimethylene-1,2,4-trisulfide (VII) was also obtained when dithiofluorenone (IV) was treated with chlorine gas and water. This compound had the same melting point as a trichlorofluorene of unknown structure obtained by Holm (14) by treating fluorene dissolved in carbon disulfide with chlorine gas. When the compound was hydrolyzed in dilute hydrochloric acid an x-chlorofluorenone, melting at 145–147°, was obtained, thus showing that two of the chlorine atoms were present as a keto-dichloride. The position of the third chlorine atom was predicted to be in either the 2- or 4- position of the fluorene nucleus, since these are the ortho and para positions to the biphenyl linkage, and meta to the carbonyl group of this compound. However, 2-chlorofluorenone is known to melt at 121–123°, having previously been prepared by Courtot (15).

The previously unknown 4-chlorofluorenone (VIII) was therefore synthesized from 4-aminofluorenone (IX), by the same series of reactions used by Huntress, Pfister, and Pfister (16) for the unequivocal synthesis of 4-bromofluorenone, and found to melt at 146–147°. A mixed melting point of the x-cholorofluorenone with VIII showed no depression, showing conclusively that treatment of dithiofluorenone and 3,5-bis-diphenylenedimethylene-1,2,4-trisulfide with chlorine gas and water yields 4,9,9-trichlorofluorene (VI).

IV

V

VI

VII

VIII

IX
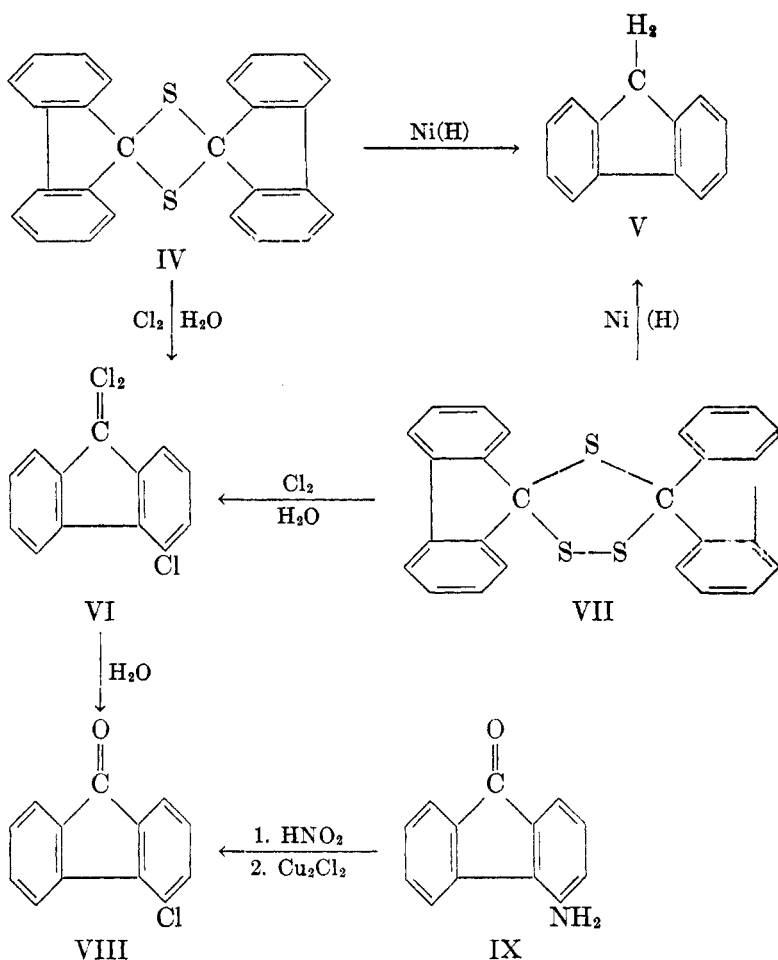
EXPERIMENTAL

The action of chlorine gas and water on 3,3,5,5-tetraphenyldimethylene-1,2,4-trisulfide.
One gram (0.00234 mole) of this trisulfide, prepared from thiobenzophenone according to
the method of Staudinger and Freudenberger (1), was suspended in 20 ml. of glacial acetic
acid and 0.504 g. (0.027 mole) of distilled water was added. Chlorine gas was bubbled
through this suspension, and the mixture shaken until the suspended material had dissolved.
The temperature of the mixture was kept below 25° during the addition of the chlorine.
About fifteen minutes were required for solution of the suspension, after which the yellow
solution was allowed to stand for two hours, and then poured over ice and immediately
extracted with ether. The ether layer was dried over magnesium sulfate, filtered, and
evaporated *in vacuo*. The colorless oil thus obtained gave an immediate precipitate of
silver chloride when treated with aqueous silver nitrate solution. This oil was hydrolyzed
by heating with water and acetic acid, and the hydrolysate extracted with ether. Evapora-
tion of the dried ether solution gave 0.83 g. of a solid compound, which on recrystallization
from alcohol yielded white needles, m.p. 46–47°. A mixed melting point with authentic
benzophenone was 46–47°. The yield of crude benzophenone was 97.8%, based on equa-
tion 3.

When the aqueous layer was treated with excess barium chloride 1.60 g. of barium sulfate was obtained, which is equivalent to 0.675 g. of sulfuric acid or 98%, based on equation 3.

The action of chlorine and water on 3,5-bis-diphenylenedimethylene-1,2,4-trisulfide. A suspension of 1 g. (0.00224 mole) of the trisulfide prepared from thiofluorenone (3) in 25 ml. of glacial acetic acid containing 0.504 g. (0.027 mole) of water was cooled in an ice-bath. Chlorine gas was introduced until the suspension had just dissolved, after which the reaction mixture was allowed to stand for one hour. The resulting clear yellow solution was poured into a mixture of ice and water and immediately extracted with ether. The ether layer was dried over magnesium sulfate and the ether removed *in vacuo*. A pale yellow solid resulted which weighed 1.2 g., gave an elemental analysis for chlorine, and melted over a wide range. Recrystallization from absolute alcohol gave a yellow crystalline compound, m.p. 147–148° which contained chlorine but gave no test for sulfur.

Anal. Calc'd for $C_{13}H_7Cl_3$: Cl, 39.46. Found: Cl, 39.17.

The crude yield was 99% on the basis of a trichlorofluorene.

The aqueous layer was treated with excess barium chloride, and 1.52 g. of barium sulfate was isolated, which is equivalent to 0.629 g. of sulfuric acid, or 97% based on equation 3.

The action of chlorine and water on dithiofluorenone. Chlorine gas was bubbled through a suspension of 0.5 g. (0.001275 mole) of dithiofluorenone (3) in 8 ml. of glacial acetic acid and 0.184 g. (0.013 mole) of water while the temperature was maintained at 20° for seven hours. The flask was then stoppered and shaken on a shaking machine until solution had taken place. The resulting solution was poured over ice and the yellow precipitate was filtered, washed with cold water, and dried over calcium chloride in a vacuum desiccator. Recrystallization from acetic acid and alcohol yielded a yellow crystalline compound melting at 147–148°. A mixed melting point with the trichlorofluorene obtained from 3,5-bis-diphenylenedimethylene-1,2,4-trisulfide showed no depression.

Hydrolysis of the trichlorofluorene. Four-tenths gram of the trichloride was boiled in a mixture of 5 ml. of acetic acid, 1 ml. of concentrated hydrochloric acid, and 15 ml. of water for four hours. An orange oil formed which solidified on standing. Several recrystallizations from alcohol gave a yellow crystalline compound, m.p. 145–147°, which was shown to be a ketone by a positive 2,4-dinitrophenylhydrazine test, and gave a positive test for chlorine. A mixed melting point with an authentic sample of 4-chlorofluorenone showed no depression.

A 2,4-dinitrophenylhydrazone of this ketone was prepared from 0.1 g. of the ketone by the usual procedure. This reaction yielded 0.185 g. (94%) of microscopic orange crystals, melting at 254–255°.

Anal. Calc'd for $C_{19}H_{11}ClN_4O_4$: N, 14.19. Found: N, 13.99.

A mixed melting point of this 2,4-dinitrophenylhydrazone with one prepared from an authentic sample of 4-chlorofluorenone showed no depression.

The action of Raney nickel on dithiofluorenone. In a 25-ml. round-bottom flask fitted with an efficient reflux condenser, 0.2 g. (0.00051 mole) of dithiofluorenone was treated with about 5 g. of Raney nickel in a mixture of absolute alcohol and sufficient benzene to dissolve the dithiofluorenone when hot. The Raney nickel was prepared according to the method of Mozingo, Wolf, Harris, and Folkers (11). After refluxing for six hours, the nickel and nickel sulfide were removed by filtration, washed with 10 ml. of benzene, and the combined filtrate and washings were placed in a separatory funnel, washed with distilled water, and finally dried over anhydrous calcium sulfate. The dry benzene solution was concentrated *in vacuo* to about 5 ml., and finally transferred to a 15 ml. weighed centrifuge tube with the aid of 5 ml. of dry benzene. Removal of the remaining benzene yielded 0.16 g. of dry solid which on recrystallization from 95% alcohol yielded 0.14 g. or 82.5%, of fluorene, m.p. 114–116°. A mixed m.p. with an authentic sample of fluorene showed no depression.

The action of Raney nickel on 3,3,5,5-tetraphenyldimethylene-1,2,4-trisulfide. In a 250-ml. flask fitted with a reflux condenser, 1 g. (0.00234 mole) of the dibenzophenone trisulfide dissolved in 70 ml. of absolute alcohol and 25 ml. of benzene was treated with 10 g. of the Raney nickel preparation. After six hours of refluxing, the nickel residue was removed by

filtration, washed with 25 ml. of benzene, and the filtrate dried over calcium chloride. The solvents were removed by distillation, and the remaining small residue transferred to a 2 ml. modified Claissen flask. The fraction that distilled between 259–263° weighed 0.67 g., which is equivalent to 85% of the theoretical amount of diphenylmethane possible. The liquid has an orange-like odor and an n_D^{23} of 1.5732. Authentic diphenylmethane has a similar odor, boils at 263°, and the refractive index, n_D^{23} is 1.5760. Further proof of the authenticity of the product was secured by oxidizing 0.3 g. (0.0018 mole) with 0.2 g. of chromic anhydride in 2 ml. of glacial acetic acid contained in a 15-ml. centrifuge tube. After two hours of refluxing the resulting dark green solution was diluted with 10 ml. of water, allowed to stand for three hours, centrifuged, and the supernatant liquid decanted. The residual white solid was washed with water, centrifuged, and recrystallized from dilute alcohol. The yield of white needles was 0.15 g. or 45%, m.p. 46–47°. A mixed m.p. with authentic benzophenone showed no depression.

The action of Raney nickel on 3,5-bis-diphenylenedimethylene-1,2,4-trisulfide. When the difluoryl trisulfide was refluxed with Raney nickel, as above, no pure products could be isolated. However, when a solution of 0.5 g. (0.00112 mole) of the trisulfide in 50 ml. of dioxane was shaken at room temperature with 6 g. of Raney nickel for twelve hours, filtered, and the filtrate and dioxane washings concentrated, a brown solid was obtained. Repeated crystallizations of this residue (with 95% alcohol) yielded about 0.05 g. of fluorene, m.p. 114–116°. A mixed m.p. with authentic fluorene showed no depression.

4-Chlorofluorenone. 4-Aminofluorenone was prepared from 2,2'-diphenic acid[3] by the method described by Huntress, Pfister, and Pfister (16). 2,2'-Diphenic acid was converted to fluorenone-4-carboxylic acid, and this compound in turn converted to the amide, and finally to the amine by the Hofmann degradation in an over-all yield of 32% based on the diphenic acid used. The sludge resulting from the addition of 2.72 g. (0.0139 mole) of 4-aminofluorenone to 20 ml. of concentrated hydrochloric acid was cooled to 0° in a salt-ice bath. The mixture was diazotized with a solution of 0.98 g. (0.014 mole) of sodium nitrite in 5 ml. of water. The diazotized solution was then added in a steady stream to a boiling solution of cuprous chloride dissolved in hydrochloric acid. After addition of the diazotized solution, the suspension of orange-yellow material was boiled for fifteen minutes, collected by suction filtration, and washed with cold water. The residue on the funnel was ground with a solution of 8 g. of sodium hydroxide in 25 ml. of water and the undissolved ketone filtered, washed free of alkali, and air-dried. The crude ketone was distilled in vacuum and the fraction that distilled to 160° at 1 mm. was twice recrystallized from absolute alcohol. The yield of long yellow needles, m.p. 147–148°, was 0.75 g. or 25%.

Anal. Calc'd for $C_{13}H_7ClO$: Cl, 16.53. Found: Cl, 16.49.

This authentic sample of 4-chlorofluorenone was readily converted to a 2,4-dinitrophenylhydrazone which melted at 254–255° after recrystallization.

SUMMARY

1. When one mole of the trisulfide produced by the action of dry air on thiobenzophenone was oxidized with chlorine and water, approximately two moles of benzophenone dichloride was formed. When the trisulfide produced by the action of dry air on thiofluorenone was oxidized in this manner, 4,9,9-trichlorofluorene was formed.

2. When one mole of the dibenzophenone trisulfide was reduced with Raney nickel, approximately two moles of diphenylmethane was formed. Likewise the difluorenone trisulfide yielded fluorene.

3. The above reactions prove that the two trisulfides are respectively, 3,3,5,5-tetraphenyldimethylene-1,2,4-trisulfide, and 3,5-bis-diphenylenedimethylene-1,2,4-trisulfide.

[3] Generously supplied by Dr. R. L. Shriner of this laboratory.

4. Dithiofluorenone yielded fluorene on reduction with Raney nickel, and 4,9,9-trichlorofluorene on oxidation with chlorine and water.

5. 4-Chlorofluorenone was synthesized in an unequivocal manner and characterized by analysis and preparation of its 2,4-dinitrophenylhydrazone.

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REFERENCES

(1) STAUDINGER AND FREUDENBERGER, *Ber.*, **61**, 1580, 1836 (1928).
(2) SCHONBERG, SCHUTZ, AND NICKEL, *Ber.*, **61**, 2175 (1928).
(3) CAMPAIGNE AND REID, *J. Am. Chem. Soc.*, **68**, 769 (1946).
(4) BARONI, *Atti Accad. Lincei*, **11**, 905 (1930).
(5) SCHOBERL, *Ann.*, **507**, 111, (1933).
(6) CONNOR, Chapt. 10, Gilman's "Organic Chemistry" 2nd Ed., John Wiley and Sons, Inc., New York, **1943**, Vol. I, p. 864.
(7) LEE AND DOUGHERTY, *J. Org. Chem.*, **5**, 81 (1940).
(8) KOHLER, *Am. Chem. J.*, **19**, 728 (1897).
(9) JOHNSON AND AMBLER, *J. Am. Chem. Soc.*, **36**, 381 (1914).
(10) GOMBERG AND BACHMANN, *J. Am. Chem. Soc.*, **69**, 248 (1927).
(11) MOZINGO, WOLF, HARRIS, AND FOLKERS, *J. Am. Chem. Soc.*, **65**, 1013 (1943).
(12) CLINE, CAMPAIGNE, AND SPIES, *J. Am. Chem. Soc.*, **66**, 1136 (1944).
(13) BERGMANN AND ISRAELASHWILI, *J. Am. Chem. Soc.*, **67**, 1951 (1945).
(14) HOLM, *Ber.*, **16**, 1082 (1883).
(15) COURTOT, *Ann. Chim.*, (10) **14**, 52 (1930).
(16) HUNTRESS, PFISTER, AND PFISTER, *J. Am. Chem. Soc.*, **64**, 2845 (1942).