polysulfide linkages, possibly cyclized, with all sulfides saturated by labile, dative-bonded sulfur atoms.

Since circumstances beyond our control have caused the complete cessation of work on this problem, proof of the structures of these products is lacking. We feel nevertheless that our results and conclusions will be of value in the literature.

Acknowledgment.—We wish to thank the Texas Gulf Sulphur Company for permission to publish these results. We are grateful to W. W. Duecker of Texas Gulf Sulphur Company and to L. H. Cretcher and W. A. Hamor of Mellon Institute for their help and advice in the research.

Summary

1. Ethylene reacted with sulfur with or without solvents or pressure to form a xylene-insoluble polymer and a soluble oil, part of which was volatile.

2. The various products were investigated and structures were postulated from the experimental evidence.

PITTSBURGH, PA. RECEIVED NOVEMBER 13, 1945

[CONTRIBUTION FROM THE BUREAU OF PLANT INDUSTRY, SOILS AND AGRICULTURAL ENGINEERING, AGRICULTURAL RESEARCH ADMINISTRATION, U. S. DEPARTMENT OF AGRICULTURE]

Molecular Rearrangement of Fluorylidene Dimethyl Sulfide to Fluorene-1-dimethyl Sulfide[1]

BY LOUIS A. PINCK AND GUIDO E. HILBERT[2]

The work of Ingold and Jessop[3] on the preparation of the unstable fluorylidene dimethyl sulfide (II) was repeated and their finding was confirmed. We have found that II rearranges in an alkaline medium such as liquid ammonia or alcoholic sodium hydroxide to fluorene-1-dimethyl sulfide (III). Reactions were carried with III involving graded oxidations, reduction and substitutions. The structure of the rearranged product was definitely established by comparing fluorenone-1-carboxylic acid (V), an oxidation product of III, with an authentic specimen obtained by the oxidation of fluoranthene.

The various compounds obtained in this study are indicated by the reaction chart.

Experimental

Rearrangement of Fluorylidene Dimethyl Sulfide (II).—A sealed glass tube containing 25 g. of I[3] and 75 cc. of liquid ammonia was kept in a steel bomb at room temperature for two weeks. After evaporating the ammonia the orange-colored solid was washed free from ammonium bromide and dried, m. p. 71–75°. It was distilled at 180–190° at 2 mm. pressure and then crystallized from 95% ethyl alcohol as white colorless needles, m. p. 77.5°,[4] yield 15.5 g. or 76.4%. The residue was a red resin.

Anal. Calcd. for $C_{15}H_{14}S$: C, 79.59; H, 6.24; S, 14.18; mol. wt., 226. Found: C, 79.31; H, 6.21; S, 14.25; mol. wt., 226, 220.

Fluorene-1-dimethyl sulfide (III) is fairly soluble in alcohol, very soluble in ether and is exceedingly stable thermally. Decomposition was effected by heating above 400° forming dimethyl sulfide and a dark brown resin.

Rearrangement was also obtained by the use of alkali but here the yield was only 28.3%. The following procedure was used. A solution of 13.5 g. of I in 180 cc. of water was treated rapidly with 100 cc. of a 30% solution of sodium hydroxide at room temperature, thereby depositing a practically colorless, finely divided precipitate. The mixture was well shaken for a few minutes and then rapidly filtered in subdued light and the solid was dried by rubbing it on a porous plate. It changed color very rapidly, first turning gray then bluish gray and finally to a permanganate-like color. It was rapidly washed into a flask with 125 cc. of absolute alcohol and treated with a solution of 35 g. of sodium hydroxide in 175 cc. of 60% alcohol. The mixture was shaken well and after keeping it in the dark for an hour it was gradually warmed to 45° in a course of two hours. With the exception of a red resin all of the solid went into solution, the latter also was red. The solution was diluted with water and extracted with benzene. The benzene soluble fraction was distilled at reduced pressure yielding 4.28 g. of impure distillate, leaving behind the major portion as a red resin. The distillate upon recrystallization from alcohol yielded 2.8 g. of III. The alcohol soluble residue was sublimed *in vacuo*, yielding 1.1 g. of yellow solid which upon further purification was identified as fluorenone.

Alcoholysis of Fluorene-1-dimethyl Sulfide (III).—A solution of 0.5 g. of III in about 15 cc. of methyl alcoholic hydrogen chloride was heated in a bomb tube at 125° for four days. Considerable pressure and a strong odor of mercaptan were noted upon opening the tube. The residue obtained upon the evaporation of the solvent melted at 56°, was purified by crystallizing it from methyl alcohol and then by sublimation, colorless needles, m. p. 58°, yield 65%. IV turned pale pink on exposure to light and became colorless when kept in the dark. It gave a negative test for sulfur by the sodium fusion method.

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.71; H, 6.71. Found: C, 85.92; H, 6.81.

Oxidation of III.—To a hot solution of 2 g. of III in 25 cc. of glacial acetic acid was slowly added 10 g. of sodium dichromate. The mixture was heated under reflux for four hours, then cooled, diluted with water, and the precipitate which deposited was removed, weight 1.45 g., m. p. 149–158°. It was dissolved in hot benzene and extracted with dilute alkali. The extract was filtered and V was precipitated by acidifying the solution, weight 0.47 g. Orange-colored needles were obtained by crystallization from benzene, m. p. 197°; mixed melting point with a specimen of fluorenone-1-carboxylic acid obtained by the oxidation of fluoranthene[5] 196–197°.

Anal. Calcd. for $C_{14}H_8O_3$: C, 74.98; H, 3.60. Found: C, 75.05; H, 3.60.

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(1) A summary of this investigation had previously been reported by Hilbert and Pinck, THIS JOURNAL, **60**, 494 (1938).

(2) Present address: Bureau of Agricultural and Industrial Chemistry, U. S. Department of Agriculture, Peoria, Illinois.

(3) Ingold and Jessop, *J. Chem. Soc.*, 713 (1930); see also Hughes and Kuriyan, *ibid.*, 1609 (1935).

(4) All melting points are corrected.

(5) Fieser and Seligman, THIS JOURNAL, **57**, 2175 (1935).

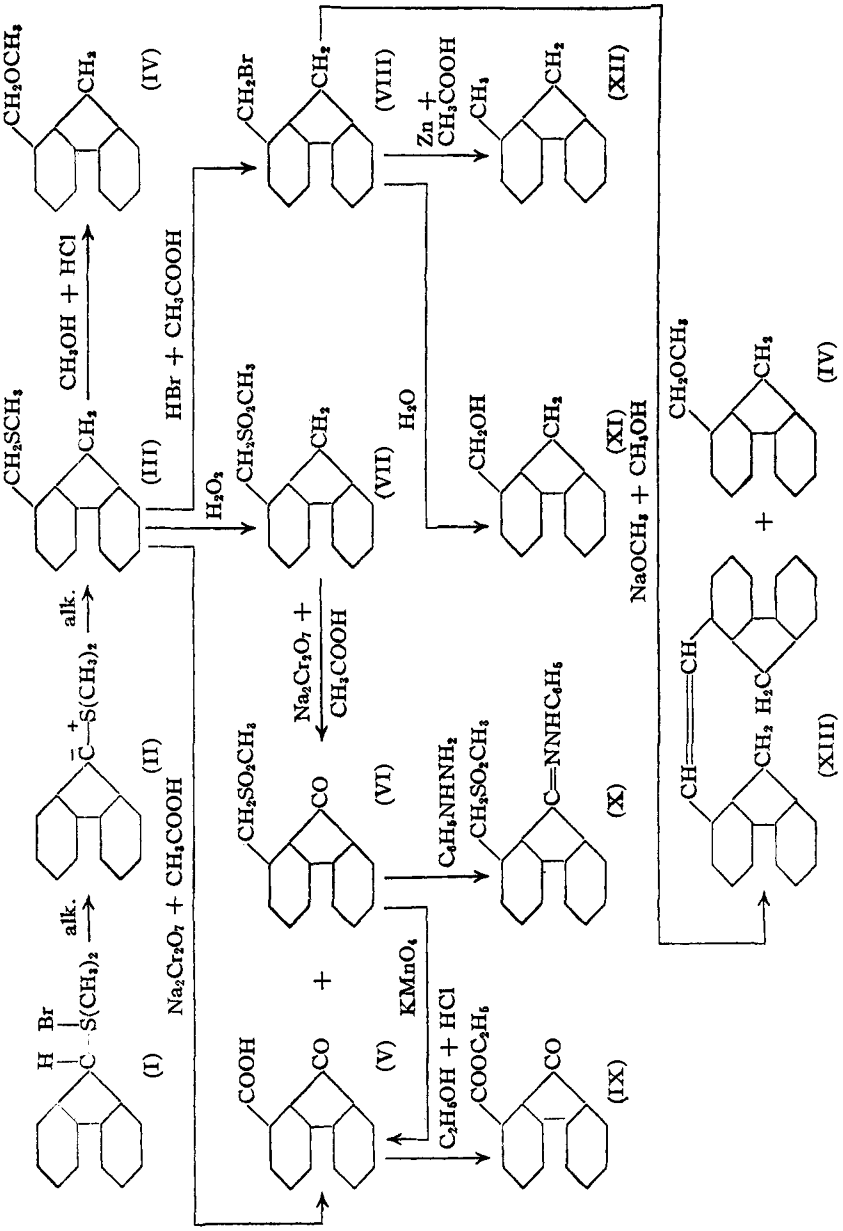

Fig. 1.—Formation and reactions of fluorene-1-dimethyl sulfide.

The **ethyl ester** IX, yellow needles, m. p. 85–86°, mixed melting point with an authentic specimen[6] unchanged.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.16; H, 4.80. Found: C, 76.34; H, 4.97.

The benzene-soluble fraction (1.21 g.) upon crystallization from *n*-propyl alcohol yielded 0.53 g. of VI.[7]

Fluorene-1-dimethyl sulfone VII was obtained by heating a solution of 3.25 g. of III in 30 cc. of glacial acetic and 6 cc. of 30% hydrogen peroxide at 100° for two hours. On cooling it yielded 2.66 g. (73%) of straw colored needles which were recrystallized from acetic acid, m. p. 192°.

Anal. Calcd. for $C_{15}H_{14}SO_2$: C, 69.77; H, 5.47; S, 12.42. Found: C, 69.78; H, 5.44; S, 12.54.

Fluorenone-1-dimethyl Sulfone (VI).—Oxidation of VII with chromic acid for two hours gave a 56.5% yield of VI and none of V.[8] The recrystallized material consisted of yellow needle-like prisms, m. p. 205°.

Anal. Calcd. for $C_{16}H_{12}SO_3$: C, 66.14; H, 4.45. Found: C, 66.23; H, 4.61.

The **phenylhydrazone** X was recrystallized from toluene, fine yellow needles, m. p. 268° (dec.).

Anal. Calcd. for $C_{21}H_{18}O_2N_2S$: C, 69.57; H, 5.01; N, 7.74. Found: C, 69.66; H, 5.22; N, 7.93.

Oxidation of 0.5 g. of VI with 2 g. of potassium permanganate in 50 cc. of water at 100° for ten hours yielded 0.09 g. of V, m. p. and mixed melting point with an authentic specimen 197°.

Fluorene-1-methyl bromide (VIII) was obtained by letting a suspension of III in a solution of 30–32% hydrobromic acid in glacial acetic acid stand for a month at room temperature in a stoppered Erlenmeyer. The solution having a very strong odor of mercaptan was taken down to dryness by suction and the residue was twice recrystallized from hexane, yielding elongated prisms, m. p. 104°. The yield in this experiment was not measured for this reaction did not go to completion.

Anal. Calcd. for $C_{14}H_{11}Br$: C, 64.86; H, 4.28; Br, 30.86. Found: C, 65.14; H, 4.37; Br, 30.58.

A practically quantitative yield of **fluorenone-1-methanol** XI was obtained by hydrolyzing VIII in a 50% aqueous acetone solution in the presence of sodium carbonate. The product consisted of clusters of fine needles when sublimed or recrystallized from hexane, m. p. 148°.

Anal. Calcd. for $C_{14}H_{12}O$: C, 85.67; H, 6.17. Found: C, 85.94; H, 6.10.

An 83% yield of **1-methylfluorene** XII was obtained by the reduction of VIII with zinc in glacial acetic acid. The product upon recrystallization from methanol yielded clusters of needles which enlarged into prisms, and prisms when sublimed, m. p. 85°.

Anal. Calcd. for $C_{14}H_{12}$: C, 93.28; H, 6.72. Found: C, 93.17; H, 6.82.

It turns yellow when exposed to sunlight for a long time possibly forming 1-methyl fluorenone.

When a methyl alcoholic solution of VIII was treated with sodium methylate a colorless precipitate of *sym*-**difluorene-1,1′-ethylene** XIII deposited within a few minutes. This was removed by filtration and recrystallized from benzene–alcohol solution, fine needles, m. p. 284–285°, yield 72%.

Anal. Calcd. for $C_{28}H_{20}$: C, 94.34; H, 5.66; mol. wt., 356. Found: C, 94.29; H, 6.03; mol. wt., 355, 347.

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[6] Goldschmidt and Lipschitz, *Monatsh.*, **25**, 1164 (1904).

[7] Its physical and chemical properties are recorded in a following experiment.

[8] Details of procedure are given in third experiment.

XIII did not readily add bromine. The methyl alcoholic filtrate of this experiment yielded 18.5% of IV when diluted with water, melting point and mixed melting point with a sample of this compound described in another experiment, 57°. This product also turned pink upon exposure to light.

Acknowledgment.—We wish to express our appreciation to Mrs. M. S. Sherman for carrying out the recorded microanalyses.

Summary

The molecular rearrangement of fluorylidene dimethyl sulfide to fluorene-1-dimethyl sulfide was effected in an alkaline medium. By graded oxidation the rearrangement product was converted into fluorene-1-dimethyl sulfone, fluorenone-1-dimethyl sulfone and fluorenone-1-carboxylic acid. The above-named acid and its ethyl ester were characterized by comparison with authentic specimens. The —SCH$_3$ group of fluorene-1-dimethyl sulfide was substituted by —OCH$_3$, —Br, —OH and —H. Fluorene-1-methyl bromide in an alcoholic solution of sodium methylate yielded *sym.*-difluorene-1,1′-ethylene and fluorene-1-dimethyl oxide.

BELTSVILLE, MARYLAND RECEIVED JANUARY 24, 1946

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE WM. S. MERRELL COMPANY]

Quaternary Ammonium Salts as Germicides. I. Non-acylated Quaternary Ammonium Salts Derived from Aliphatic Amines[1]

BY R. S. SHELTON, M. G. VAN CAMPEN, C. H. TILFORD, H. C. LANG, L. NISONGER, F. J. BANDELIN[2] AND H. L. RUBENKOENIG

The antibacterial properties of quaternary ammonium compounds were first observed toward the end of the last century among the carbonium dyestuffs, such as auramin,[3] methyl violet[3] and malachite green.[4] These types of compounds are effective chiefly against the Gram-positive organisms. Later Jacobs and Heidelberger[5] studied the antibacterial activity of substituted hexamethylenetetrammonium salts. In the nineteen-twenties Browning, *et al.*, found greater and somewhat less selective bactericidal powers among styryl and anil quinolinium salts,[6] the flavine dyes[7] and quaternary derivatives of pyridine, quinoline, acridine and phenazine.[8] Hartman and Kagi[9] observed antibacterial activity in quaternary ammonium compounds of acylated alkylene diamines. With the disclosure by Domagk[10] of the much improved germicidal activity obtained when a large aliphatic residue was attached to the quaternary nitrogen atom, the study of the use of quaternary ammonium salts as germicides was greatly stimulated. In the past ten years many patents have been issued in the field, but few reports have been published of systematic study of these compounds and of the influence of their chemical structure upon their antibacterial properties. We wish to record here the work done in this Laboratory on this problem.

There was first prepared a series of simple aliphatic quaternary ammonium salts of the general type R(CH$_3$)$_3$NBr, where R is a straight chain alkyl group of 6 to 18 carbon atoms. These compounds, when pure, are obtained as fine white, nearly odorless, crystals. In general they are nearly insoluble in diethyl ether and benzene, sparingly soluble in acetone, and, except for the stearyl derivative, freely soluble in water and alcohol. They are stable in acid solution and in all but very strongly alkaline solutions. Table I shows the effect upon germicidal activity of variations in the chain length of the R group.

To determine the effect of the anion upon the activity, the following cetyltrimethylammonium salts were prepared: the chloride, bromide, iodide, nitrate, sulfate, methosulfate, secondary orthophosphate, acetate, benzoate, cyanide, laurate, hydrocinnamate, salicylate and fluosilicate. The phosphate, laurate and salicylate gave definitely lower activity; no significant differences in germicidal power were observed among the other salts, except that the halides and the sulfate gave slightly higher activity against *Staph. aureus* than did the other salts. The solubility in water of the series varied from about 1:4 to 1:10, except for the iodide and the laurate, whose solubilities were 1:2000 and 1:250, respectively.

Similar compounds were prepared in which one or more of the N-methyl groups were replaced by other radicals. In Table II is shown the effect of these substitutions upon antibacterial activity.

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(1) This series of papers was presented in part at the September, 1939, meeting of the American Chemical Society, in Boston, and at the April, 1940, meeting in Cincinnati.

(2) Present address: Flint, Eaton and Company, Decatur, Illinois.

(3) Stilling, "Anilifarbstoffe als Antiseptica und ihre Anwendung in der Praxis," Trubner, Strassburg, 1890.

(4) See and Moreau, *Bull. gen. Therap.*, **120**, 502 (1891).

(5) Jacobs and Heidelberger, *Proc. Nat. Acad. Sci. U. S.*, **1**, 226 (1915); *J. Biol. Chem.*, **20**, 659 (1915); *J. Exptl. Med.*, **23**, 569 (1916).

(6) Browning, Cohen, Ellingworth and Gulbransen, *Proc. Roy. Soc.*, London, **100B**, 293 (1926).

(7) Browning, Gulbransen, Kennaway and Thornton, *Brit. Med. J.*, **1**, 73 (1926).

(8) Browning, Cohen, Gaunt and Gulbransen, *Proc. Roy. Soc.*, London, **93B**, 329 (1922).

(9) Hartman and Kagi, *Z. angew. Chem.*, **4**, 127 (1928).

(10) Domagk, *Deut. med. Wochschr.*, **61**, 829 (1935).