

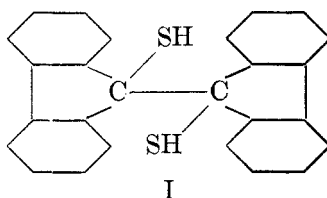
2-THIOFLUORENOL

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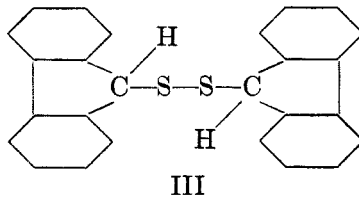
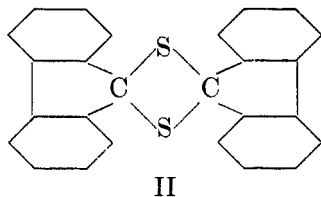
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Nearly all of the work on sulfur compounds of fluorene up to present has dealt with derivatives of the 9-carbon atom, although a few aromatic sulfonic acids are known.

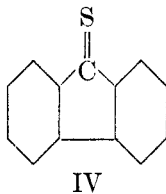
Several of the divalent sulfur compounds contain two fluorene nuclei. As early as 1904 Manchot and Krische (1) prepared 9,9'-bifluorenyl-9,9'-dithiol, I.



In the following year Smedley (2) prepared a compound which she called thiofluorenone and to which she assigned structure II, but Bergmann and Hervey (3) showed that Smedley's compound contained active hydrogens and that its structure should be represented by III. They prepared II by the passage of

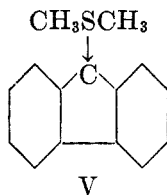


hydrogen sulfide and hydrogen chloride into fluorenone for 15 hours. Recently Campaigne and Reid (4) obtained monomeric thiofluorenone, IV, by interrupting the process after three hours. They reported it to be an unstable green solid melting at 75-76°. Bergmann and Hervey also prepared 9,9'-difluorenylsulfide by the action of sodium hydrosulfide on 9-chlorofluorene.



Schonberg, Schutz, and Peter (5) synthesized 9-phenylthiofluorene and the mercaptol type compound, 9-phenylthio-9-*o*-nitrophenylthiofluorene. Several similar mercaptol compounds have been reported (7, 8).

Ingold and Jessup (6) prepared fluorylidenedimethylsulfide, V, which contains a semipolar bond between sulfur and carbon.

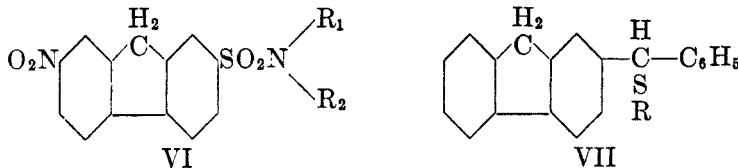


Wedekind and Strusser (9) obtained 9-fluorenesulfonic acid from 9-chlorofluorene with sodium bisulfite. Ordinarily, sulfuric acid acts on fluorene to produce first fluorene-2-sulfonic acid, and then fluorene-2,7-disulfonic acid (10, 11, 12).

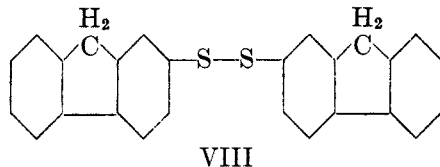
Suter (13) suggests that subsequent sulfonic acid groups would go to positions 3 and 6. Consideration of the nitration products (14), however, makes it seem more probable that the 4 and 5 positions would be involved, as these are ortho to the linkage between the phenyl rings and meta to the first sulfonic acid groups.

Courtot prepared fluorene-2-sulfonyl chloride and the amide (15), as well as 7-nitrofluorene-2-sulfonic acid; while Ray and MacGregor (16) prepared a number of derivatives of the type VI.

Fluorylphenylmethyl thioethers of type VII were used by Ray and Levine (17) in the elucidation of the sulfonium mechanism.



Since 2-thiofluorenol had not been reported, we decided to attempt its preparation. By the reduction of fluorene-2-sulfonyl chloride with iodine and red phosphorus we obtained mostly 2,2'-difluoryl disulfide, VIII, melting at 179–180°, but some low-melting material (m.p. 122°) was isolated also.



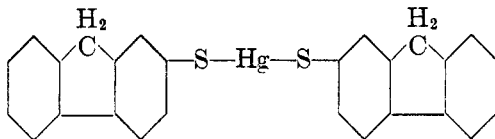
Sodium sulfide failed to reduce the disulfide linkage, while phosphorus pentabromide gave a compound containing bromine in the ring.

With sodium in anhydrous ammonia we obtained a red solid that dissolved in water. On the addition of hydrochloric acid a yellow compound having an indefinite melting point (75–120°) precipitated. This could not be purified to a sharply melting compound and the analytical results were low for 2-thiofluorenol.

The benzoyl derivative, however, melted sharply at 172–173° and gave correct analytical results.

We then turned to the method whereby fluorene-2-sulfonyl chloride was reduced with zinc dust and acetic acid, but the product obtained (m.p. 122°) did not have the expected properties. It was not readily soluble in sodium hydroxide and the analysis for sulfur was 12.86 instead of the calculated 16.15. It did not give a benzoate.

If this compound were the sulfinic acid, mercuric chloride should cause the substitution of HgCl for SO₂H. Instead, when the compound was boiled with mercuric chloride, the mercury salt of 2-thiofluorene, IX, resulted. It melted at 235–237° and was analytically pure.



IX

To obtain the free thiol, hydrogen sulfide was passed into an alcoholic suspension of the mercury salt. The resulting 2-thiofluorene melted at 111–113° and the analytical results obtained for sulfur showed it to be somewhat impure. It was, however, readily soluble in alkali, although oxidation soon took place in this medium. Hydrogen peroxide gave the disulfide, VIII, in practically quantitative yields, while the pyridine solution on standing in air gave the disulfoxide.

Inasmuch as we were not completely satisfied with the method of preparation and had not identified the compound originally obtained (m.p. 122°) we decided to prepare 2-thiofluorene by another method. We treated fluorene-2-diazonium chloride with potassium ethylxanthate and decomposed the addition compound in hot water. On hydrolysis and recrystallization we obtained pure 2-thiofluorene melting at 129° compared with the previous melting point 111–113°.

The mercury salt and the benzoate were identical with those previously obtained. When the thiol was boiled with acetic anhydride, the compound melting at 122° and having 13% sulfur was obtained. It was thus shown to be the acetate, formed by acetylation during the reduction in glacial acetic acid.

EXPERIMENTAL

All melting points uncorrected.

Fluorene-2-sulfonyl chloride was prepared by Courtot's method (15) but was recrystallized (15 g.) from a mixture (55 cc.) of 3:1 acetic acid-acetic anhydride. It melted at 162°.

Reduction with iodine and phosphorus. Ten grams of fluorene-2-sulfonyl chloride was placed in 300 cc. of 80% acetic acid with 10 g. of red phosphorus and then 8 g. of iodine was added slowly. About 2–3 cc. of concentrated sulfuric acid was added to the mixture after 2 hours. Following 5 hrs. refluxing, the solution was filtered and allowed to stand overnight. An electrophoric powder precipitated. On recrystallization from acetic acid 4.5 g., 60%, of 2,2'-difluorenyl disulfide, m.p. 180°, was obtained in the form of a white powder.

Anal. Calc'd for C₂₈H₁₈S₂; S, 16.20; Mol. Wt., 394.

Found: S, 16.18, 16.54; Mol. Wt. (benzene), 363.

This compound was also obtained by the oxidation of 2-thiofluorenel with hydrogen peroxide in acetic acid.

Reduction with zinc dust. To 200 cc. of hot anhydrous acetic acid was added 10 g. (0.038 mole) of fluorene-2-sulfonyl chloride. The solution was cooled to 40° and 16 g. (0.24 mole) of zinc dust was added. The temperature rose to 80°. Then 5 cc. of concentrated sulfuric acid was added and the mixture refluxed for an hour. It was filtered, poured into water, and the precipitate recrystallized from alcohol. The fluorene-2-thiol acetate melted at 122° and was soluble in cold benzene, chloroform, and ethyl acetate, and in hot alcohol.

Anal. Calc'd for $C_{18}H_{12}OS$: S, 13.3; Eq. Wt., 240.

Found: S, 12.86; Eq. Wt., 231.

The equivalent weight was determined by boiling for 1 hr. in an excess of standard alkali and then titrating with standard acid.

Fluorene-2-diazonium chloride was prepared from 2-aminofluorene (18, 19). It crystallized in golden-yellow needles melting with decomposition at 120°.

2-Thiofluorenel. Two 800-ml. beakers were placed in an ice-salt bath. One contained a solution of 7 g. of potassium ethylxanthate in 100 cc. of water; in the other, 10 g. of fluorene-2-diazonium chloride was suspended in 200 cc. of water. A few cc. of the diazonium chloride was added to the xanthate solution, and a tan, curdy precipitate formed. This was removed in small quantities from the solution and quickly dropped into a beaker containing 25 cc. of boiling water. Nitrogen was explosively evolved and the resulting product existed as a heavy dark brown oil on the surface of the water. More of the diazonium chloride was added to the potassium ethylxanthate and the process continued as above until all the diazonium salt had reacted. The product was allowed to cool, separated from the water, and dissolved in 250 cc. of ether. It was then washed with four 100-cc. portions of 5% NaOH, two 100-cc. portions of 5% HCl, and two 100-cc. portions of water. After standing overnight over calcium sulfate the ether was evaporated. The dark brown tar was hydrolyzed by refluxing for 5 hours with 15 g. of KOH dissolved in 50 cc. of water and 100 cc. of alcohol. The solution was filtered hot and the alcohol evaporated. The potassium salt of the thiol was a reddish brown powder which readily dissolved in water. On the addition of 25 cc. of dilute sulfuric acid to the water solution, the crude orange colored thiol precipitated. This was filtered by suction and when dry melted at 58-62°. On heating with alcohol, the thiol dissolved leaving a brown tar which was removed. Water was added to the solution bringing down a yellow precipitate which melted at 98°. Several recrystallizations with 150-cc. portions of 2:1 alcohol-water mixtures, and boiling with Darco gave 2.6 g. of a pale yellow product melting at 108-112°. It was difficult to purify the 2-thiofluorenel further; however, after numerous purifications, small white crystals melting at 127-129° were obtained.

Anal. Calc'd for $C_{18}H_{10}S$: S, 16.15; Mol. Wt., 198.

Found: S, 16.06, 16.12; Mol. Wt. (camphor), 185.

Mercury salt of 2-thiofluorenel. Three g. of 2-thiofluorenel was dissolved in 200 cc. of alcohol and filtered hot through a charcoal mat. To this clear solution 3 g. of mercuric chloride in hot alcohol was added, and a bright yellow precipitate resulted. The reaction mixture was cooled with constant shaking over a period of ½ hour; the product melted at 217-219°. After several recrystallizations from Cellosolve, the constant melting point 235-237° was obtained.

Anal. Calc'd for $C_{26}H_{18}S_2Hg$: Hg, 33.71. Found: Hg, 33.41.

Fluorene-2-thiol benzoate. One and one-half g. of 2-thiofluorenel was added to 100 cc. of boiling 6 N sodium hydroxide. After boiling for about a minute a soap-like tan substance formed. This was cooled and 5 cc. of benzoyl chloride added with stirring. The solution was filtered and on standing overnight yellow crystals came down. When dry they melted at 142°. After several recrystallizations from ethyl alcohol a product melting at 172-173° was obtained.

Fluorene-2-thiol acetate. Approximately 0.5 gram of 2-thiofluorenel was dissolved in 5 cc. of acetic anhydride and brought to a boil. The solution was cooled in an ice-bath and 5 cc. of 6 N sodium hydroxide and a little ice were added. After constant shaking over a

period of 15 minutes a yellow precipitate came down (m.p. 102–108°). After several recrystallizations from the minimum of alcohol, a product melting at 120–122° was obtained.

Anal. Calc'd for $C_{15}H_{12}OS$: S, 13.3. Found: S, 12.97.

A mixed melting point with the material obtained by the reduction of fluorene-2-sulfonyl chloride with zinc dust in glacial acetic acid showed them to be identical.

Reduction of 2,2'-difluoryl disulfide. Three grams of the disulfide was dissolved in 150 cc. of anhydrous ammonia and small pieces of metallic sodium added until the characteristic blue color persisted. When the ammonia had evaporated, the mass was dissolved in water and acidified. The crude material was recrystallized from dilute alcohol but could not be obtained pure (m.p. 100–110°).

Anal. Calc'd for $C_{13}H_{10}S$: S, 16.15. Found: S, 15.55.

It was converted to the benzoate with benzoyl chloride and dilute sodium hydroxide. From 1.5 g. of thiol there was obtained 1.3 g. of fluorene-2-thiol benzoate. On recrystallization to the constant m.p. 173°, 1 g. or 65% was obtained.

Anal. Calc'd for $C_{19}H_{14}OS$: S, 10.59. Found: S, 10.28.

2,2'-Difluoryldisulfoxide. One g. of 2-thiofluorene-2-thiol was boiled with pyridine, filtered, and the clear solution allowed to stand in air for 12 hours. A yellow compound precipitated. On recrystallization from Methyl Cellosolve there was obtained 0.4 g. melting at 217°.

Anal. Calc'd for $C_{26}H_{18}O_2S_2$: S, 15.02; Mol. Wt., 426.

Found: S, 14.90, 14.96; Mol. Wt. (camphor), 468.

SUMMARY

2-Thiofluorene and its derivatives; the acetate, the benzoate, the mercury salt; and 2,2'-difluoryl disulfide and 2,2'-difluoryldisulfoxide have been prepared and characterized.

2-Thiofluorene has been prepared both by the reduction of fluorene-2-sulfonyl chloride and by the reaction of fluorene-2-diazonium chloride with potassium ethylxanthate.

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