The bond energies reflect the enhanced stability of the carbonyl group as the hydrogens in formaldehyde are replaced by alkyl groups.

If the energy differences are taken as a measure of the hyperconjugation effect then these carbonyl compounds should be placed in the following order for decreasing electrophilic power: formaldehyde > other aldehydes > ketones.[15] This is the observed decreasing order for the per cent. of "abnormal" products; formaldehyde yielding only abnormal products, other aldehydes both "normal" and "abnormal" products and ketones only "normal" products.

The variation of the electrophilic property of the carbonyl group in going from acetaldehyde to its higher homologs should be much less pronounced than for the change formaldehyde to acetaldehyde. Although the hyperconjugative power of alkyl groups has been placed in the order Me > Et > Pr^{β} > Bu^{γ} (which correlates small differences in reaction rates),[16] the effect is too small to make a significant variation in thermochemical data.[17] The theory of hyperconjugation would predict the following order for decreasing electrophilic powers: *i*-butyraldehyde > propionaldehyde > acetaldehyde but the differences might easily be masked by some other effect. Evidently, although propionaldehyde gives a higher per cent. of "abnormal" product than does acetaldehyde, the higher homologs give a lower proportion of "abnormal" product. And α-substituted aldehydes give particularly low yields of the "abnormal" product. The trend suggests that a steric effect is superposed on the electrical effect and causes the variation.

(15) For a discussion of the dipole moments of carbonyl compounds in terms of hyperconjugation see E. C. Hurdis and C. P. Smyth, THIS JOURNAL, **65**, 89 (1943).

(16) E. D. Hughes, C. K. Ingold and N. A. Taber, *J. Chem. Soc.*, 949 (1940).

(17) G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 54.

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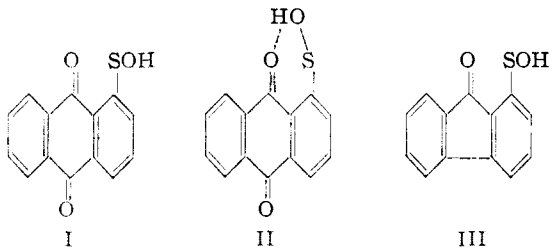
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Derivatives of Sulfenic Acids. V. 1-Fluorenone Sulfur Compounds[1]

BY NORMAN KHARASCH AND THOMAS C. BRUICE

In an earlier paper, it was suggested that hydrogen bonding might be responsible for the unique stabilization of 1-anthraquinonesulfenic acid. As one approach to testing this hypothesis, the synthesis of the structural analog, 1-fluorenonesulfenic acid, was attempted. This objective was, however, not attained; and the conclusion is made that the isolation of 1-fluorenonesulfenic acid and its salts is precluded by the predominant tendency of these substances to disproportionate to 1-fluorenonyl disulfide and 1-fluorenonesulfinic acid. An entire series of 1-fluorenone sulfur compounds has, however, been synthesized, and several interesting similarities and differences between these compounds and their 1-anthraquinone analogs are noted. Some improvements in the synthesis of 1-aminofluorenone and the 1-halofluorenones are described.

In 1912, Fries[2] reported the successful isolation of 1-anthraquinonesulfenic acid (I) and certain of its salts. Since then, however, all attempts to find other sulfenic acids—in the anthraquinone series,[3,4] as well as in the benzene series[5-9]—have not been successful. In contrast, in the less extensively investigated selenium analogs, three selenenic acids (ArSeOH) have been reported.[10] Interest in the sulfenic acids, as such, is thus enhanced by the unique isolation of the single member of this class (I), by the contrasting existence of corresponding selenenic acids, and by the circumstance that—in spite of their non-isolation—free sulfenic acids have very frequently been invoked as intermediates in studies concerned with the chemistry and biochemistry of various classes of organic sulfur compounds.[11]



I II III

In a recent review,[11] it was suggested that the stabilization of 1-anthraquinonesulfenic acid may be caused by hydrogen bonding as shown in structure II. As a first step in testing this hypothesis, it was desired to establish whether a similar stabilization would be observed in 1-fluorenonesulfenic acid (III). The work in the fluorenone series was therefore patterned closely on that in the anthraquinone series.

Fries accomplished the isolation of 1-anthraquinonesulfenic acid by converting methyl 1-anthraquinonesulfenate to potassium 1-anthraquinonesulfenate (by treatment with potassium hydroxide), then liberating the free sulfenic acid from the salt by the action of acetic acid.[12] When methyl 1-fluorenonesulfenate was treated similarly, however, we obtained only 1-fluorenonyl disulfide

(1) This paper is based on an undergraduate research thesis submitted by Thomas C. Bruice.

(2) K. Fries, *Ber.*, **45**, 2965 (1912).

(3) K. Fries and G. Schürmann, *ibid.*, **52**, 2170 (1919).

(4) K. Fries and G. Schürmann, *ibid.*, **52**, 2182 (1919).

(5) T. Zincke and J. Baeumer, *Ann.*, **416**, 86 (1918).

(6) T. Zincke and K. Eismayer, *Ber.*, **51**, 751 (1918).

(7) T. Zincke and F. Farr, *Ann.*, **391**, 55 (1912).

(8) T. Zincke and S. Lenhardt, *ibid.*, **400**, 1 (1913).

(9) T. Zincke and H. Röse, *ibid.*, **406**, 103 (1914).

(10) O. Behaghel and co-workers, *Ber.*, **65**, 812 (1932); **66**, 708 (1933); **68**, 1540 (1935); **72**, 582, 697 (1939). For a brief review of this work see reference 11, pp. 277–278.

(11) N. Kharasch, S. J. Potempa and H. L. Wehrmeister, *Chem. Rev.*, **39**, 269 (1946).

(12) The original work of Fries on 1-anthraquinonesulfenic acid was confirmed in this Laboratory by Mr. Albert T. Fowler.

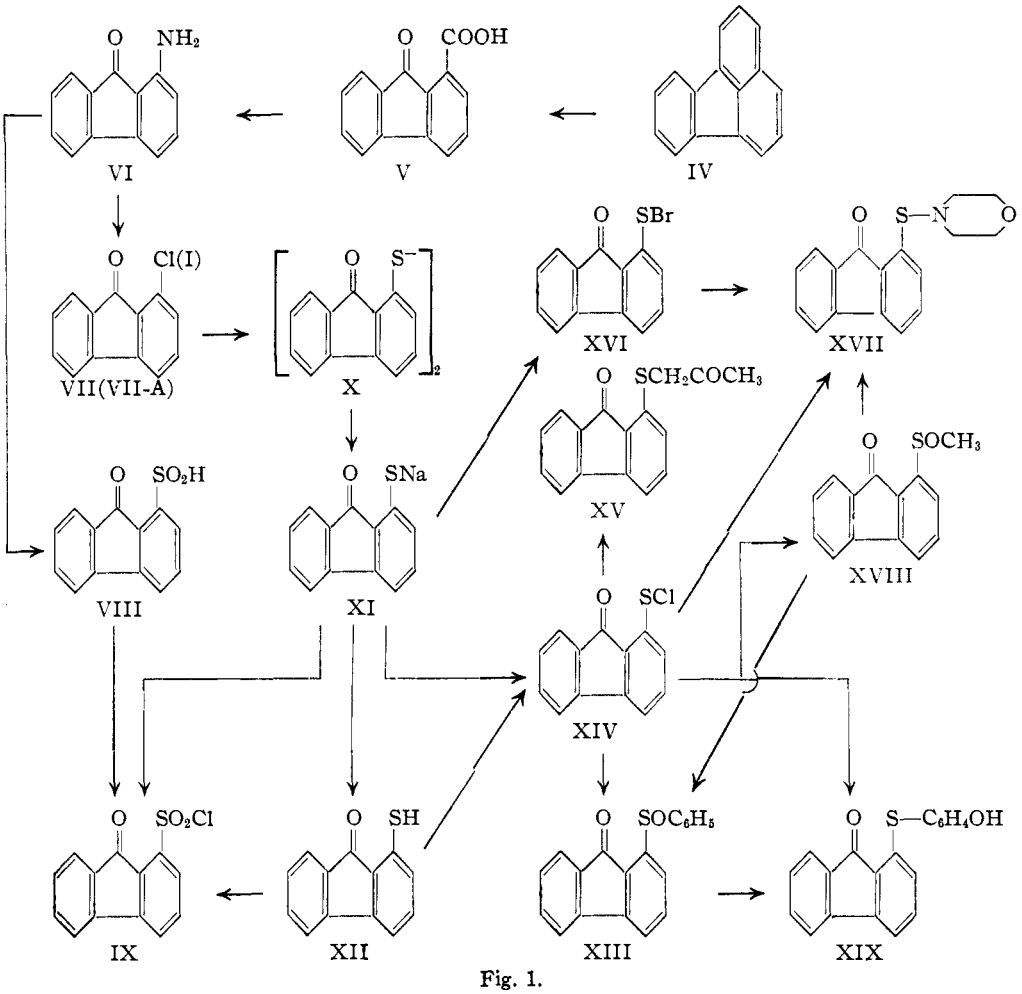


Fig. 1.

and 1-fluorenonesulfinic acid in amounts which suggest the reactions (Ar = 1-fluorenonyl)

$$2ArSOCH_3 + 2HOH \longrightarrow 2[ArSOH] + 2CH_3OH \quad (1)$$

$$2[ASOH] \longrightarrow ArSO_2H + ArSH \quad (2)$$

$$ArSH + ArSOCH_3 \longrightarrow ArSSr + CH_3OH \quad (3)$$

$$3ArSOCH_3 + 2HOH \longrightarrow ArSO_2H + ArSSAr + 3CH_3OH$$

Because of its great insolubility, the disulfide could be isolated in quantitative yield, whereas the sulfinic acid was obtained in 88% of the quantity expected on the basis of the above equations, Equations (1) and (2) are, of course, hypothetical, but the immediate and quantitative formation of the disulfide by reaction of 1-fluorenonethiol and the methyl sulfenate (equation 3) was actually observed.

While the isolation of 1-fluorenonesulfenic acid was not achieved in this study, a complete series of the heretofore unrecorded 1-fluorenone sulfur compounds was prepared. The synthetic sequence and various conversions which were effected in the present study are summarized in Fig. 1.

Fluorenone-1-carboxylic acid (V) and its amide were prepared by recorded procedures.[13,14] The procedure of Huntress, *et al.*,[14] for conversion of the amide to 1-aminofluorenone (VI) *via* the Hofmann reaction was, however, modified to permit greater convenience in preparing larger quantities of the amine. The directions recorded in the experimental section were arrived at by determining the effect of temperature of reaction and concentration of hypohalite (both hypobromite and hypochlorite) on yield of amine. Sodium hypochlorite proved to be the more suitable reagent; and by its use, 60–70% yields of pure 1-aminofluorenone were obtained conveniently,

1-Fluorenonesulfinic acid (VIII) was prepared by reaction of diazotized 1-aminofluorenone with sulfur dioxide in the presence of copper powder. This sulfinic acid, a new and exceptionally stable member of its class, was readily obtained as a pale-yellow solid which could be stored indefinitely without decomposing.

Although some sulfenyl bromides (for example, 1-anthraquinonesulfenyl bromide) may be prepared by reaction of the sulfinic acid and hydrogen bromide in glacial acetic acid (equation 4),[4,15]

$$ArSO_2H + 3HBr \longrightarrow ArSBr + 2H_2O + Br_2 \quad (4)$$

1-fluorenonesulfinic acid (VIII) could not thus be converted to 1-fluorenonesulfenyl bromide (XVI). The product obtained instead was 1-fluorenonyl disulfide (X). This corresponds to the similar

(13) L. F. Fieser and A. M. Seligman, THIS JOURNAL, **57**, 2174 (1935).

(14) E. H. Huntress, K. Pfister and K. H. T. Pfister, *ibid.*, **64**, 2846 (1942).

(15) K. Fries and G. Schürmann, *Ber.*, **47**, 1195 (1914).

formation of disulfides from certain sulfinic acids (for example, benzenesulfinic acid) studied by Fries and Schürmann.[15]

To obtain 1-chlorofluorenone and 1-iodofluorenone (VII, VII-A) by the Sandmeyer reaction from the amine, the procedure of Huntress, Pfister and Pfister[14] was modified. By diazotizing 1-aminofluorenone in glacial acetic acid, rather than in aqueous solution, the formation of the diazonium salt occurs more smoothly and the subsequent reaction with cuprous halide is facilitated, leading to 80% crude yields of 1-chlorofluorenone and even higher yields (97%) of 1-iodofluorenone. These yields are considerably above those of 40–50% of comparable crude products recorded in the literature.[14]

1-Fluorenonyl disulfide (X) was synthesized from 1-chlorofluorenone or 1-iodofluorenone by refluxing with sodium disulfide in 50% aqueous dioxane for 60 hours, and the disulfide was then reduced with sodium hydrosulfide to the sodium salt of 1-fluorenonethiol (XI), which was readily converted to 1-fluorenonethiol by acidification. It may be noted that the conditions required to reduce 1-fluorenonyl disulfide to the thiol are much more rigorous, possibly because of the greater insolubility of the disulfide, than are those described for the corresponding reaction of 1-anthraquinonyl disulfide.[2] Alkaline cleavage of 1-fluorenonyl disulfide in aqueous dioxane also yielded 60% of the thiol; but the reduction with sodium hydrosulfide is the better method for synthesis of the thiol. The isolation of thiol in 60% yield by cleavage of the disulfide with alkali suggests, however, that in this reaction, also, one may postulate the intermediate formation of the sulfenic acid, and its disproportionation to thiol and sulfinic acid; simple hydrolytic cleavage could only give a maximum yield of 50% of thiol.

In contrast to the known halogenolysis of 1-anthraquinonyl disulfide to 1-anthraquinonesulfenyl chloride or bromide, 1-fluorenonyl disulfide failed to undergo similar reactions. Attempts to catalyze the halogenolysis of 1-fluorenonyl disulfide —by methods similar to those of Kharasch, Gleason and Buess[16] for the halogenolysis of 2,4-dinitrophenyl disulfide—were not effective. 1-Fluorenonesulfenyl chloride (XIV) and the corresponding bromide (XVI) were, however, obtained in excellent yields *via* reactions of the halogens with 1-fluorenonethiol under anhydrous conditions. The sulfenyl halides (as well as the thiol, its sodium salt, the disulfide and 1-fluorenonesulfinic acid) yielded 1-fluorenonesulfonyl chloride (IX) as the product of reaction with chlorine in moist acetic acid.

1-Fluorenonesulfenyl chloride (as well as the bromide) yielded 1-fluorenonesulfenomorpholide (XVII) by reaction with morpholine; and with sodium ethoxide, these sulfenyl halides formed methyl 1-fluorenonesulfenate (XVIII). The latter also yielded the morpholide (XVII) by reaction with morpholine. This conversion of the methyl ester of 1-fluorenonesulfenic acid to the sulfenamide is not unexpected, but the number of such recorded conversions appears to be very small (*cf.*, for example, ref. 11, p. 318).

1-Fluorenonyl disulfide was invariably the major product isolated in attempts to obtain methyl 1-fluorenonesulfenate by direct reaction of the sulfenyl chloride or bromide with methanol. This failure to yield the methyl sulfenate by direct reaction with methanol is another distinguishing feature between the sulfenyl halides in the 1-fluorenone series and those of the 1-anthraquinone analogs. 1-Fluorenonesulfenyl chloride did, however, react directly with acetone to form acetonyl 1-fluorenonyl sulfide (XV); whereas in the reaction of 1-fluorenonesulfenyl bromide with acetone, only 1-fluorenonyl disulfide was obtained. 1-Fluorenonesulfenyl bromide also differs from the sulfenyl chloride (m.p. 189.5–190°) by decomposing at 155–160°, without melting, to form 1-fluorenonyl disulfide.

Refluxing the methyl ester (XVIII) with excess phenol, dissolved in benzene, gave a separable mixture of the water-insoluble phenyl 1-fluorenonesulfenate (XIII) and an isomeric, water-soluble 1-fluorenonyl hydroxyphenyl sulfide[17] (XIX). Phenyl 1-fluorenonesulfenate (XIII) was converted (Fries-type rearrangement) to XIX, by refluxing in benzene solution; and XIX was also synthesized by reaction of 1-fluorenonesulfenyl chloride with phenol.

Experimental[18]

1-Aminofluorenone.—To 20 g. (0.09 mole) of powdered fluorenone-1-carboxamide,[14] there was added a solution of sodium hypochlorite (prepared by passing 7 g. (0.01 mole) of chlorine into a mixture of 180 g. of cracked ice, 180 ml. of water and 20 g. (0.5 mole) of sodium hydroxide). The reaction mixture was stirred at 40° for one hour, 50 ml. of 10% sodium hydroxide was added, and the mixture was refluxed for one-half hour, chilled and filtered. The solid residue was thoroughly extracted with ether in a soxhlet apparatus, and the crystals obtained by removal of the ether from the extract were recrystallized from hot isopropyl alcohol, giving 11–13 g. (65–75%) of crude product, m.p. 113–117°. This was redissolved in hot isopropyl alcohol, diluted with a large quantity of warm water to definite turbidity, and permitted to crystallize slowly; yield 10.5–12.3 g. (60–70%); m.p. 118° (lit.[14] 118.5°).

1-Fluorenonesulfinic Acid.—1-Aminofluorenone (6 g., 0.031 mole) was dissolved in a mixture of 45 ml. of glacial acetic acid, 5 ml. of water and 10 ml. of 96% sulfuric acid. Purified dioxane[19] (100 ml.) was added, with vigorous stirring, to form a suspension. This was cooled to 5°, 2.13 g. (0.031 mole) of sodium nitrite in 5 ml. of water was added, and the mixture stirred for 15 minutes to ensure complete diazotization. It was then saturated with sulfur dioxide, by passing a stream of the gas into the reaction mixture for one hour at 5°. To the stirred mixture, finely ground copper powder was added during 20 minutes at 5°. Addition of copper was then continued, at room temperature for ten minutes and while the reaction mixture was heated to boiling at the rate of 1° per minute. (The quantity of copper added does not appear to be critical; 6 to 10 g. was used in various runs.) The hot mixture was filtered, and the residue was aggregated with additional precipitate obtained by diluting the filtrate with 700 ml. of cold water. A thin aqueous slurry of the total solids was made slightly basic by adding warm concentrated sodium hydroxide solu-

(16) N. Kharasch, G. I. Gleason and C. M. Buess, THIS JOURNAL, **72**, 1796 (1950).

(17) This compound is most likely the *p*-hydroxyphenyl isomer, but the exact position of the hydroxyl group was not established in this study.

(18) Melting points reported are not corrected. Microanalyses were performed by Dr. A. Elek of the Elek Microanalytical Laboratory, Los Angeles, California.

(19) K. Hess and H. Frahm, *Ber.*, **71**, 2627 (1938).

tion and the suspension was filtered. The filtrate was clarified by stirring with about 1 g. of charcoal for 30 minutes, filtered, acidified with acetic acid, and refiltered to remove a dark precipitate. Acidification of the filtrate with concentrated hydrochloric acid formed a voluminous precipitate, which was collected, redissolved in aqueous sodium hydroxide, acidified with acetic acid, filtered, and reprecipitated with concentrated hydrochloric acid. The product was washed with small portions of cold water and desiccated; 5.13 g., 70%.

Anal. Calcd. for $C_{13}H_8O_3S$: C, 63.93; H, 3.30. Found: C, 63.85; H, 3.30.

Various samples of the acid decomposed at 162–163° if the bath was heated slowly; a sharp value of 170° was observed by introducing the sample into the bath at 160° and heating at the rate of 1° per minute.

1-Fluorenonesulfinic Acid with Hydrogen Bromide in Glacial Acetic Acid.—1-Fluorenonesulfinic acid (100 mg.) was dissolved in 10 ml. of boiling glacial acetic acid, and into the solution (at 15° in some runs or 70° in others) there was passed a rapid stream of dry, bromine-free hydrogen bromide. The precipitated product was shown to be 1-fluorenonyl disulfide by its decomposition temperature and reduction, with sodium hydrosulfide, to 1-fluorenonethiol. Attempts to isolate the desired 1-fluorenonesulfenyl bromide from the mother liquor by evaporation *in vacuo*, by dilution with petroleum ether or by cooling were all unsuccessful.

1-Chlorofluorenone.—1-Aminofluorenone (7.8 g., 0.04 mole) was dissolved in 160 ml. of glacial acetic acid. Concentrated hydrochloric acid (24 ml.) was added, the mixture was stirred for one-half hour, and 40 ml. of water was added. The solution was cooled to 2° and diazotized by adding, below its surface, in the course of ten minutes, 3.61 g. (0.052 mole) of sodium nitrite in 40 ml. of water. The diazotization mixture was stirred for eight minutes, 0.8 g. of urea was added, stirred for eight minutes more, and added during 15 minutes to a boiling solution of 15.6 g. of cuprous chloride in 160 ml. of 6 *N* hydrochloric acid. The resulting suspension was boiled vigorously and allowed to stand overnight. The crystalline product was collected, washed with 400 ml. of water and dried. Various runs yielded 6.87–7.70 g. (80–90%) of 1-chlorofluorenone, m.p. 133–134°. Recrystallization from aqueous alcohol gave a product, m.p. 135–136°, which was sufficiently pure for use in further work. Further recrystallization and vacuum sublimation raised the melting point to 137–137.8°, in accord with the value of Huntress[14] for a similarly purified sample.

1-Iodofluorenone.—1-Aminofluorenone (7.8 g., 0.04 mole) was diazotized as above, and the diazotization mixture was added slowly to a solution of 66.4 g. (0.4 mole) of potassium iodide in 200 ml. of water. After standing one hour, the mixture was heated slowly to 90° to digest the precipitate. The crude 1-iodofluorenone was thoroughly washed with water, dissolved in dioxane, reprecipitated by adding alkaline potassium iodide solution, washed again, and dried at 90°; yield 11.9 g., 97.5%; m.p. 140–142°, raised to 144–145° by vacuum sublimation. The sublimed product, after dissolving in a mixture of methanol–dioxane and reprecipitation with water, melted at 147–148° (lit.[14] 146.5–147°). The product melting at 140–142° was equally suitable in the synthesis of 1-fluorenonyl disulfide as was the 1-chlorofluorenone melting at 135–136°.

1-Fluorenonyl Disulfide.—Sodium disulfide solution was prepared from 4.8 g. (0.02 mole) of sodium sulfide nonahydrate, an equivalent (0.64 g.) of sulfur and 40 ml. of 50% aqueous dioxane. To this there was added 2.15 g. (0.01 mole) of 1-chlorofluorenone (or 0.01 mole of 1-iodofluorenone), the mixture was heated at 90–100° for 60 hours, and any 1-fluorenonethiol formed was oxidized to disulfide by adding iodine–potassium iodide solution. The dark precipitate was thoroughly washed with water, extracted with acetone for six hours in a soxhlet apparatus, and the unextracted residue was recrystallized from a minimum of hot nitrobenzene, washed with small portions of dioxane and dried at 110°; yield 1.7 g. (70%); m.p. 335–336° (dec.).

Anal. Calcd. for $C_{26}H_{14}O_2S_2$: C, 73.90; H, 3.33. Found: C, 73.73; H, 3.35.

Sodium Salt of 1-Fluorenonethiol.—Sodium hydroxide (0.19 g., 0.005 mole) in 3 ml. of absolute ethanol was added to a suspension of 1 g. (0.02 mole) of 1-fluorenonyl disulfide in 50 ml. of ethyl cellosolve. The mixture was saturated with hydrogen sulfide gas while being slowly heated to boiling, and this procedure was repeated several times to assure complete reaction. The solution was cooled, filtered, concentrated to 25 ml. and diluted with 200 ml. of ligroin (Skellysolve C). The product was collected, dissolved in minimum hot 95% ethanol, filtered, reprecipitated by adding ligroin, and dried; brick-red plates, 0.98 g.; dec. 135–145°. Acidification of aqueous solutions of the sodium salt precipitated free 1-fluorenonethiol (see below).

1-Fluorenonethiol.—The solution obtained by reducing 4.8 g. of 1-fluorenonyl disulfide with sodium hydrosulfide (as above) was evaporated to dryness, 300 ml. of water was added, the mixture was filtered, acidified with concentrated hydrochloric acid and refrigerated. The thiol was collected, dissolved in aqueous potassium hydroxide and reprecipitated by acidifying the filtered solution. The dried product (88–90%) was a pale-yellow powder, m.p. 113–115°; it was entirely suitable for conversion to 1-fluorenonesulfenyl chloride. Dissolving the product in a minimum of hot benzene, filtering, and diluting the filtrate with twice the volume of *n*-hexane produced long, yellow needles of the thiol, m.p. 117–118°.

Anal. Calcd. for $C_{13}H_8OS$: C, 73.53; H, 3.80. Found: C, 73.47; H, 3.91.

1-Fluorenonethiol was also obtained as follows. 1-Fluorenonyl disulfide (2.0 g.) and potassium hydroxide (2 g.) were suspended in a mixture of 40 ml. of diethyl cellosolve and 5 ml. of ethanol. The mixture was refluxed for one hour, filtered, acidified with 10 ml. of concentrated hydrochloric acid and refrigerated. The crude product was dried in air and extracted with a refluxing mixture of equal volumes of Skellysolve C and benzene, with some solid calcium chloride present to remove residual water. The extract was filtered, and the extraction of the residue repeated. Refrigeration of the combined filtrates gave 1.2 g. (60%) of 1-fluorenonethiol, m.p. 114–116°. Recrystallization, as above, gave golden needles, m.p. 117–118°.

1-Fluorenonesulfenyl Chloride.—Carbon tetrachloride (50 ml.) was saturated with chlorine at 0°, and 2.34 g. (0.01 mole) of the sodium salt of 1-fluorenonethiol was added slowly to the cold solution. The mixture was warmed gently to expel excess chlorine, heated to boiling, and filtered. The residue was extracted with boiling carbon tetrachloride; the extract and original filtrate were combined, successively frozen at −65° and thawed at −10° to induce crystallization, and the product collected and dried *in vacuo*. Concentration of the mother liquors, and similar freezing and thawing produced successive crops of crystals; total product, 1.2 g. (50%), m.p. 175–180°. The sulfenyl chloride was characterized by conversion to acetonyl 1-fluorenonyl sulfide (see below).

A more convenient synthesis of 1-fluorenonesulfenyl chloride was achieved. The thiol (5 g., 0.02 mole) was dissolved in excess, warm carbon tetrachloride, and the solution was filtered, dried by azeotropic distillation and cooled to 0°. A volume of dry carbon tetrachloride equal to that used to dissolve the thiol was saturated with chlorine at 0°; and the dissolved thiol was added to it slowly, with stirring. The mixture was warmed to a gentle simmer, refrigerated, and the long yellow needles were collected and dried. Additional product was obtained by concentrating and refrigerating the filtrate, giving a total of 5.5–5.6 g. (93–95%) of 1-fluorenonesulfenyl chloride, m.p. 186–187°. Recrystallization from carbon tetrachloride raised the melting point to 189.5–190°.

Anal. Calcd. for $C_{13}H_7OSCl$: C, 63.28; H, 2.86. Found: C, 63.47; H, 3.05.

1-Fluorenonesulfenyl Bromide.—To 7.8–8.0 g. of bromine in 50 ml. of anhydrous carbon tetrachloride was added 1 g. (0.0047 mole) of 1-fluorenonethiol in 50 ml. of carbon tetrachloride. The mixture was refrigerated, giving a brown precipitate which turned orange when washed with small portions of carbon tetrachloride. The filtrate and washings yielded a second crop of orange crystals; total yield 1.16 g. (85%). The 1-fluorenonesulfenyl bromide decomposes at 155–160°, changing from orange to yellow, and with accompanying sublimation. The residue decomposed at 325–335°, marked by charring and melting. Undoubtedly, the sulfenyl bromide decomposes to form the disulfide and bromine.

1-Fluorenonesulfonyl Chloride.—Either the disulfide, thiol, sulfinic acid or sulfenyl chloride was placed in about twenty volumes of a saturated solution of chlorine in glacial

acetic acid at 0°. The mixture was warmed, the solvent aspirated at room temperature, and the yellow residue dissolved in about four volumes of hot dioxane. Dilution with two volumes of ethanol, filtration and cooling led to a nearly quantitative yield of the sulfonyl chloride in each case. This was recrystallized from 50% benzene–dioxane, m.p. 209–210°.

Anal. Calcd. for $C_{13}H_7O_3SCl$: C, 56.00; H, 2.53. Found: C, 56.27; H, 2.70.

Acetonyl 1-Fluorenonyl Sulfide.—Reaction of the sulfenyl chloride with excess acetone, in benzene solution at 50°, was carried out during half an hour. Isolation and recrystallization from acetone yielded yellow needles, m.p. 159.5°.

Anal. Calcd. for $C_{16}H_{12}O_2S$: C, 71.61; H, 4.51. Found: C, 71.64; H, 4.66.

Methyl 1-Fluorenonesulfenate.—To 1.175 g. (0.0047 mole) of 1-fluorenonesulfenyl chloride in 50 ml. of dry benzene, an equivalent (0.257 g.) of sodium methoxide in anhydrous methanol was added. The mixture was heated to near boiling and the solvent aspirated. The residue was extracted with hot benzene, the mixture was filtered, and the filtrate was diluted with *n*-hexane, concentrated and refrigerated; yield of product, 1.06 g. (92%); m.p. 75–77°. Several recrystallizations from mixtures of benzene and *n*-hexane raised the melting point to 79–80°. Methyl 1-fluorenonesulfenate was also obtained in the above manner from 1-fluorenonesulfenyl bromide; but it could not be obtained by direct reaction of the sulfenyl chloride and methanol. 1-Fluorenonyl disulfide was formed instead.

Anal. Calcd. for $C_{14}H_{10}O_2S$: C, 69.40; H, 4.16. Found: C, 69.30; H, 4.27.

Hydrolysis of Methyl 1-Fluorenonesulfenate.—Numerous attempts were made to determine whether potassium 1-fluorenonesulfenate could be obtained by hydrolysis of methyl 1-fluorenonesulfenate. In all of these, the rapid precipitation of 1-fluorenonyl disulfide was observed. The following is a typical example. To 100 mg. (0.004 mole) of methyl 1-fluorenonesulfenate in 5 ml. of absolute methanol, at 40°, 0.13 ml. (0.008 mole) of 6.2 *N* aqueous potassium hydroxide was added. Reaction occurred immediately, with formation of a yellow precipitate. The mixture was allowed to stand for 15 minutes, then warmed on the steam-bath. The precipitate was collected, washed with methanol and dried at 100° (60 mg., m.p. 335–336° dec.). The typical decomposition temperature, physical appearance, and conversion of aggregated product (by reduction with sodium hydrosulfide) to 1-fluorenonethiol, m.p. 117–118°, all agree with the conclusion that the product is 1-fluorenonyl disulfide. The 60 mg. of disulfide obtained in this run corresponds to a quantitative recovery, in accord with equation 1–3 given in the introduction to this paper.

The filtrate and washings from recovery of the disulfide were concentrated *in vacuo* to small volume, acidified with acetic acid, and filtered. There was no precipitation at this stage, but addition of 0.2 ml. of concentrated hydrochloric acid, and chilling, led to a yellow crystalline product (30 mg. after drying in an evacuated pistol with phosphorus pentoxide). In its mode of isolation, acid character, physical appearance and typical decomposition, this product compared identically with authentic 1-fluorenonesulfinic acid. Formation of a typical, bright emerald-green color in an ethanolic solution of the product to which excess concentrated alkali was added also coincided with a behavior observed for the authentic sulfinic acid. The 30 mg. of product corresponds to 88% of the quantity of sulfinic acid expected on the basis of equation 1–3.

1-Fluorenonyl Disulfide *via* Methyl 1-Fluorenonesulfenate and 1-Fluorenonethiol.—To 85 mg. (0.0004 mole) of 1-fluorenonethiol, in 10 ml. of 50% benzene–absolute methanol, a similar solution of 100 mg. (0.0004 mole) of methyl 1-fluorenonesulfenate was added. The precipitate which formed immediately was washed with warm alcohol and dried at 100°; yield 170 mg. (100%) of 1-fluorenonyl disulfide, m.p. 335–336° (dec.).

1-Fluorenonesulfenomorpholide.—An excess of dry morpholine, dissolved in anhydrous benzene, was added to 100 mg. of 1-fluorenonesulfenyl chloride (or equivalent amounts of the sulfenyl bromide or the methyl sulfenate) dissolved in dry benzene. The mixture was warmed, the solvent evaporated, and the residue extracted with benzene to separate the sulfenomorpholide from the morpholine hydrochloride. The benzene extract was diluted with petroleum ether, refrigerated, the product collected and recrystallized from dioxane–water mixture, giving 80–90% of 1-fluorenonesulfenomorpholide, m.p. 172–173°.

Anal. Calcd. for $C_{17}H_{15}O_2SN$: C, 68.66; H, 5.09. Found: C, 68.36; H, 5.23.

Reaction of Methyl 1-Fluorenonesulfenate with Phenol.—Methyl 1-fluorenonesulfenate (242 mg., 0.001 mole) and 4.7 g. (0.05 mole) of phenol, in 10 ml. of anhydrous benzene, were refluxed for eight hours. The solvent and excess phenol were aspirated at 90°, the residue treated with excess dilute potassium hydroxide solution, and the alkaline suspension was filtered to remove undissolved phenyl 1-fluorenonesulfenate. The filtrate was acidified with hydrochloric acid, and the 1-fluorenonyl *p*-(?)-hydroxyphenyl sulfide was collected, dried and recrystallized from benzene—diluted with *n*-hexane. Yields: phenyl 1-fluorenonesulfenate, 118 mg. (39%); 1-fluorenonyl *p*-(?)-hydroxyphenyl sulfide 137 mg. (45%). After several recrystallizations from cold benzene and *n*-hexane, the sulfide melted at 237–238° and the sulfenate at 250–252°. The products are readily distinguished by the solubility of the sulfide in aqueous alkali.

Anal. Calcd. for $C_{19}H_{12}O_2S$: C, 74.78; H, 3.87. Found: for phenyl 1-fluorenonesulfenate: C, 74.98; H, 4.09. Found: for 1-fluorenonyl *p*-(?)-hydroxyphenyl sulfide: C, 75.04; H, 4.09.

On refluxing phenyl 1-fluorenonesulfenate in benzene for several hours, the ester was partially converted to the hydroxyphenyl sulfide. The mixture could be separated by treatment with alkali and the reflux process repeated, using the unreacted phenyl 1-fluorenonesulfenate. This suggests that, in the reaction of methyl 1-fluorenonesulfenate with phenol, the phenyl sulfenate is a precursor of the hydroxyphenyl sulfide, the latter being formed by a Fries-type rearrangement of the former. Similar rearrangements of aryl sulfenate esters have been noted by other workers.[11]

1-Fluorenonyl *p*-(?)-Hydroxyphenyl Sulfide from 1-Fluorenonesulfenyl Chloride and Phenol.—A solution of 1-fluorenonesulfenyl chloride (247 mg., 0.001 mole) and 94 mg. of phenol (0.001 mole), in benzene, was refluxed for 20 hours, then filtered, concentrated and refrigerated. The crude product was collected, dissolved in dilute potassium hydroxide solution, filtered, reprecipitated by acidification, and dried. Recrystallization from benzene–*n*-hexane mixture gave 220 mg. (72%) of pure 1-fluorenonyl *p*-(?)-hydroxyphenyl sulfide, m.p. 237–238°.

LOS ANGELES, CALIF. RECEIVED DECEMBER 26, 1950