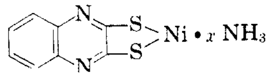
Anal. Calc'd. for $C_{12}H_{14}N_2S$: C, 66.06; H, 6.42. Found: C, 66.20; H, 6.43.

Quinoxaline-2,3-dithiol was ethylated by digesting 1 g. of the thiol with 3 g. of sodium hydroxide in 50 ml. of 95% alcohol, then adding 5 ml. of ethyl iodide and refluxing for $1^1/_2$ hours. The solvents were evaporated and the material was treated as described above. The yield of white product, which melted at 48–50°, was 84.6%.

The *2,3-di-(ethylthio)quinoxaline* was also prepared from 2,3-dichloroquinoxaline and sodium ethyl mercaptide. To an alcohol solution of 5 ml. (0.068 mole) of ethyl mercaptan was first added 0.6 g. (0.026 mole) of sodium and then 1.7 g. (0.0085 mole) of the dichloroquinoxaline. The solution was refluxed for 5 hours, cooled, diluted with water, and the mixture was distilled until most of the alcohol was removed. On cooling, the remaining oil was extracted with ether and the ether solution was evaporated. The residue was extracted with petroleum ether, decolorized with charcoal, and evaporated. The oil crystallized, forming 1.72 g. of product or 80.5%. This substance, recrystallized several times from acetone-water, had m.p. 50–51°. The mixture m.p. was 49–50°.

Anal. Calc'd for $C_{12}H_{14}N_2S_2$: C, 57.60; H, 5.60; S, 25.60. Found: C, 57.78; H, 5.76; S, 25.38.

Nickel derivative. The addition of an ammoniacal nickel solution to the yellow solution of quinoxaline 2,3-dithiol in concentrated ammonium hydroxide gave a dark red liquid. Concentrated solutions formed a crystalline precipitate at once. This substance was washed with NH_4OH and air-dried. If the non-volatile residue from combustion analysis was assumed to be Ni_3O_4, then the formula of the nickel complex would probably be:



Anal. Calc'd for hexamine $C_8H_{22}N_8NiS_2$: C, 27.22; H, 6.24; Ni, 16.64; Calc'd for tetramine $C_8H_{16}N_6NiS_2$: C, 30.11; H, 5.02; Ni, 18.41. Found: C, 28.09; H, 4.57; Ni, 18.1.

When the crystalline Ni derivative was digested with hot water, it hydrolyzed to an amorphous *magenta*-colored flocculent substance of great coloring power. This is probably a *lake*, since it showed a high Ni content and little organic matter.

Analysis of the air-dried product: C, 3.81; H, 2.74; Ni, 55.56.

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The Synthesis and Some Reactions of 9-Fluorenyl Nitrate[1]

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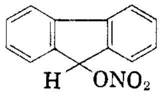
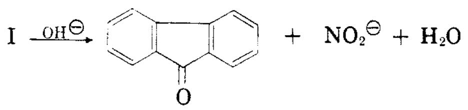
Interest in the hydrolytic and thermal decomposition of nitrate esters has led recently to the synthesis of benzhydryl nitrate,[2,3,4] triphenylmethyl nitrate,[3,4,5] and tri-(*p*-nitrophenyl)methyl nitrate.[6] Of these the first two are extremely sensitive towards hydrolysis and are very difficult to obtain in a pure form. It has now been found that 9-fluorenyl nitrate (I), a structural analog of benzhydryl nitrate, may be prepared easily and that it is stable to hydrolysis and decomposition during storage. It was prepared by the action of silver nitrate on 9-bromofluorene in acetonitrile,[7] and is a white crystalline solid which can be purified readily by crystallization.



I

A cursory examination of the reactions of 9-fluorenyl nitrate with acid and base has been made. When the compound was dissolved in methanolic potassium hydroxide, a deep yellow color immediately appeared and crystals of fluorenone (II) were deposited; no fluorenol was found. Thus this nitrate ester appears to undergo alkaline hydrolysis exclusively by the α-hydrogen elimination process[8,2] yielding the ketone and nitrite ion. Other nitrate esters which hydrolyze in base exclusively by this process are trichloroethyl nitrate,[9] α-nitratoketones,[10] and the nitrobenzyl nitrates.[2] These results indicate that the acidity of the α-hydrogen atom may be the determining factor in the α-elimination process thus suggesting that the transition state for this process is close to reactants. However, it still has not been determined whether the process is concerted or involves a discrete carbanion intermediate and thus the contribution of the carbonyl forming reaction to the transition state is unknown.[11]



II

When 9-fluorenyl nitrate was dissolved in 95% sulfuric acid, a deep blue green color appeared. When the sulfuric acid solution of the nitrate ester was poured into water, 9-fluorenol was formed. It thus appears that this nitrate ester is solvolyzed to the 9-fluorenyl carbonium ion (blue-green color) in strong acid. The same color was generated when 9-fluorenol was dissolved in sulfuric acid.

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[1] This research was carried out under Army Ordnance Contract W-01-021-ORD-334.

[2] Baker and Heggs, *J. Chem. Soc.*, 616 (1955).

[3] Merrow and Boschan, *J. Am. Chem. Soc.*, **76**, 4622 (1954).

[4] Cheeseman, *Chemistry & Industry*, 281 (1954).

[5] Cristol and Leffler, *J. Am. Chem. Soc.*, **76**, 4468 (1954).

[6] Hawthorne, *J. Am. Chem. Soc.*, **77**, 5523 (1955).

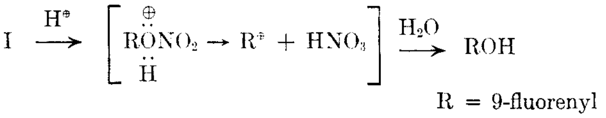
[7] Ferris, McLean, Marks, and Emmons, *J. Am. Chem. Soc.*, **75**, 4078 (1953).

[8] Baker and Easty, *J. Chem. Soc.*, 1207 (1952).

[9] Emmons, McCallum, and Freeman, *J. Org. Chem.*, 19, 1472 (1954).

[10] Emmons and Freeman, *J. Am. Chem. Soc.*, **77**, 4415 (1955).

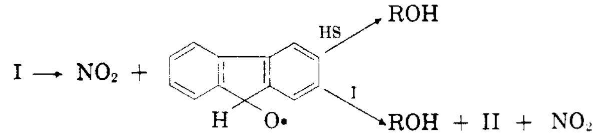
[11] For a more detailed consideration of the α-elimination reaction, see ref. 2, p. 623.



$$I \xrightarrow{H^{\oplus}} \left[\overset{\oplus}{\underset{H}{RONO_2}} \rightarrow R^{\oplus} + HNO_3 \right] \xrightarrow{H_2O} ROH$$

R = 9-fluorenyl

The thermal decomposition of 9-fluorenyl nitrate was examined also. 9-Fluorenol and small amounts of fluorenone were obtained when the ester was heated in boiling chlorobenzene for several hours. This reaction appears to involve homolysis of the ester to the 9-oxyfluorene radical (III) which then extracts a hydrogen atom from the solvent or from another molecule of nitrate ester.



III

There was no evidence for the β-cleavage process generally followed by simple alkyl nitrates[12] and by triphenylmethyl nitrate.[5] In such a case o-phenylbenzaldehyde would have been produced.

The stability of 9-fluorenyl nitrate and the clean-cut character of its reactions would seem to make it an ideal subject for mechanistic investigations of the reactions of aralkyl nitrates.

EXPERIMENTAL

9-Fluorenyl nitrate. A solution of 5.1 g. (0.03 mole) of dry silver nitrate in 15 ml. of anhydrous acetonitrile was added all at once to a solution of 4.9 g. (0.02 mole) of 9-bromofluorene[13] in 100 ml. of anhydrous acetonitrile. The mixture was allowed to stand at room temperature with occasional shaking for two hours. The precipitated silver bromide was removed by filtration and the filtrate was treated with a few milliliters of methyl iodide to destroy the excess silver nitrate. The solution was refiltered and the solvent was removed from the filtrate by evaporation under reduced pressure to produce a pale yellow solid; yield, 4.4 g. (97%). Recrystallization from petroleum ether (40–60°) yielded a mat of white needles, m.p. 90–91°. The infrared spectrum of this material had characteristic nitrate ester bands at 1640 and 1272 cm^{-1}.

Anal. Calc'd for $C_{13}H_9NO_3$: C, 68.72; H, 3.99; N, 6.17. Found: C, 69.18; H, 3.63; N, 5.87.

Reaction of 9-fluorenyl nitrate with acid. To 15 ml. of 95% sulfuric acid was added 0.2 g. of 9-fluorenyl nitrate. A deep blue green color appeared as the solid dissolved. This solution was poured on ice and the white solid that separated was collected and recrystallized from petroleum ether, m.p. 154–155°. 9-Fluorenol melts at 156°.[14] This alcohol produced the same deep blue green color when dissolved in 95% sulfuric acid.

Reaction of 9-fluorenyl nitrate with base. To 10 ml. of a 10% solution of potassium hydroxide in methanol was added 0.5 g. of 9-fluorenyl nitrate. The solution took on a deep yellow color and yellow crystals were slowly deposited. These crystals were removed by filtration and recrystallized from ethanol, m.p. 82–84°. Fluorenone melts at 83–83.5°.[14] No fluorenol was found even after extraction of the basic solution with ether and evaporation of these extracts.

Thermal decomposition of 9-fluorenyl nitrate. A solution of 0.8 g. of fluorenyl nitrate in 60 ml. of dry chlorobenzene was heated at 125–130° under a stream of dry nitrogen for six hours. The exit gases were passed into a 10% ferrous ammonium sulfate solution. A small amount of black precipitate formed during the heating period indicating the presence of nitric oxide. After the heating period was complete the solution was concentrated to 10 ml. and placed on an Activity I neutral alumina column and eluted with benzene followed by methylene chloride. Fifteen 250-ml. fractions were taken. The first benzene extract contained a trace of unreacted starting material. The next four gave 0.1 g. of fluorenone (identified by comparison of its infrared spectrum with that of an authentic sample). The next four fractions (benzene) contained no material. The last six fractions (methylene chloride) yielded 0.4 g. of fluorenol, m.p. 154–155°.

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[12] Boschan, Merrow, and Van Dolah, *Chem. Revs.*, **55**, 495 (1955).

[13] Sampey and Reid, *J. Am. Chem. Soc.*, **69**, 234 (1947).

[14] Heilbron, *Dictionary of Organic Compounds*, Oxford University Press, New York, N. Y., 1953, Vol. II, p. 545.

The Infrared and Ultraviolet Absorption Spectra of 9-*aci*-Nitrofluorene[1]

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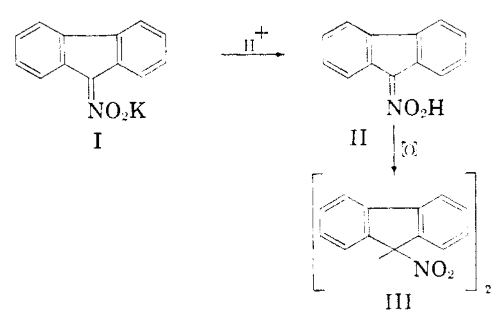
Although the existence of *aci*-nitroparaffins is well established, nothing has been reported concerning their absorption spectra. Since such spectra are inherently interesting because of the unique system involved, the infrared and ultraviolet spectra of 9-*aci*-nitrofluorene (II), a stable *aci*-nitro compound, have been measured.

It was believed[2] for many years that 9-nitrofluorene existed in both a labile *aci*-form and a stable nitro form. However, it was established conclusively in 1930[3] that the material obtained upon acidification of potassium 9-fluorenenitronate (I) is indeed 9-*aci*-nitrofluorene, and that this compound cannot be isomerized to the 9-nitro compound. Rather it is easily oxidized to the dimeric nitro compound, 1,2-dinitro-1,2-bidiphenyleneëthane (III).



This latter compound previously had been assigned the structure of 9-nitrofluorene.[2] The unusual sta-

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[1] This research was carried out under Army Ordnance Contract W-01-021-ORD-334.

[2] Wislicenus and Waldmüller, *Ber.*, **41**, 3334 (1908).

[3] Nenitzescu and Isacescu, *Ber.*, **63**, 2484 (1930).