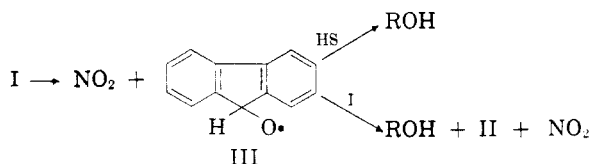


The thermal decomposition of 9-fluorenyl nitrate was examined also. 9-Fluorenol and small amounts of fluorenone were obtained when the ester was heated in boiling chlorobenzene for several hours. This reaction appears to involve homolysis of the ester to the 9-oxyfluorene radical (III) which then extracts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



There was no evidence for the β -cleavage process generally followed by simple alkyl nitrates¹² 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-bromofluorene¹³ 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 $\text{C}_{15}\text{H}_9\text{NO}_3$: 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°. 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°. No fluorenol was found even after extraction of the basic solution with ether and evaporation of these extracts.

(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.

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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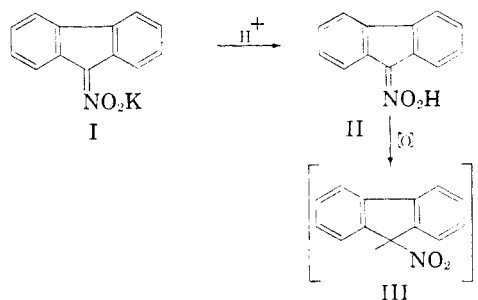
The Infrared and Ultraviolet Absorption Spectra of 9-*aci*-Nitrofluorene¹

JEREMIAH P. FREEMAN AND KEITH S. MCCALLUM

Received November 17, 1955

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 believed² for many years that 9-nitrofluorene existed in both a labile *aci*-form and a stable nitro form. However, it was established conclusively in 1930³ 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-bidiphenyleneethane (III).



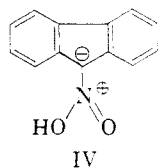
This latter compound previously had been assigned the structure of 9-nitrofluorene.² The unusual sta-

(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).

bility of this *aci*-nitro compound is undoubtedly due to the large contribution of structures such as IV to the ground state of the molecule. The tendency to establish this non-classical aromatic system accounts for other unusual effects in the fluorene



system such as the acidity of fluorene itself, the reactivity of bidiphenyleneethylene toward Grignard reagents,⁴ and the stability of the enol of 9-formylfluorene.⁵

The infrared spectrum (Fig. 1,A) of 9-*aci*-nitrofluorene possesses several significant features. There are no bands attributable to a hydroxyl

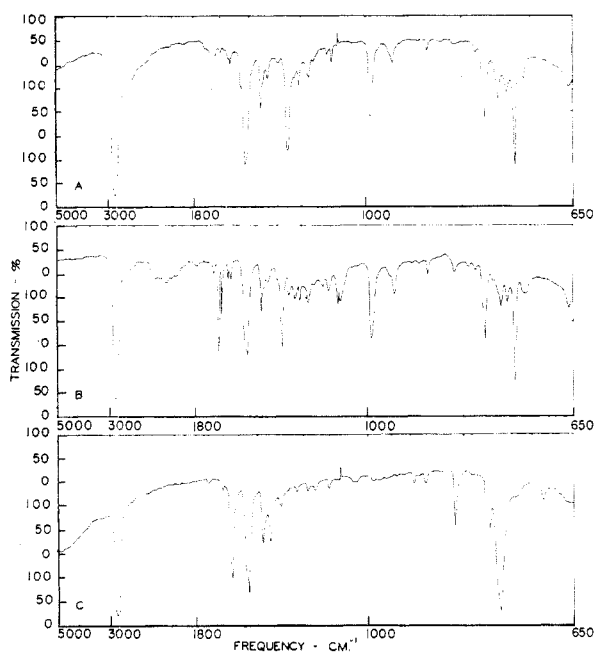


FIG. 1.—INFRARED ABSORPTION SPECTRA OF: A, 9-*aci*-nitrofluorene; B, *aci*-d-9-nitrofluorene; C, 1,2-dinitrobidiphenyleneethane.

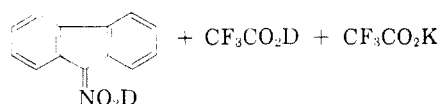
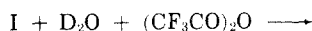
group or to a weakly associated hydroxyl group above 3100 cm^{-1} . The carbon-hydrogen stretching band, however, has a broadened appearance similar to that found in fatty acid dimers. There is no strong band in the $1500\text{--}1600\text{ cm}^{-1}$ region where nitro group absorption is found, but there is a band at 1652 cm^{-1} which may be attributed to the presence of a carbon-nitrogen double bond. In the out-of-plane carbon-hydrogen bending region (13μ), the spectrum of 9-*aci*-nitrofluorene is not typical of *o*-disubstituted phenyl rings as is that of the dinitro compound III (Fig. 1,C) which has a very strong

(4) Fuson and Porter, *J. Am. Chem. Soc.*, **70**, 895 (1948).

(5) Wislicenus and Waldmüller, *Ber.*, **42**, 785 (1909); Wislicenus and Russ, *Ber.*, **43**, 2719 (1910).

band at 743 cm^{-1} . The spectrum of the dinitro compound also shows typical absorption for an aliphatic nitro group at 1540 cm^{-1} .

Since the spectrum of 9-*aci*-nitrofluorene suggested that it exists as a dimer in which the hydrogen atoms are shared equally between two oxygen atoms, the corresponding deuterium compound was synthesized for comparison. It was prepared by adding trifluoroacetic anhydride to a solution of potassium 9-fluorenenitronate in deuterium oxide. The *aci*-nitro compound precipitated immediately. The broad band in the 5μ region of its spectrum (Fig. 1,B) may be attributed to the associated oxygen-deuterium stretching vibrations. An inter-



esting feature is that the carbon-nitrogen double bond has been shifted to 1622 cm^{-1} . Attempts to obtain molecular weight data in order to confirm the spectral indication of dimer formation were frustrated by the insolubility of the *aci*-nitro compound in non-polar solvents. Its molecular weight measured in dioxane indicated that the compound was monomeric in that solvent.

The ultraviolet spectrum (Fig. 2) of 9-*aci*-nitrofluorene is similar in general shape to that of fluorenone⁶ and fluorenone oxime⁶ and quite different

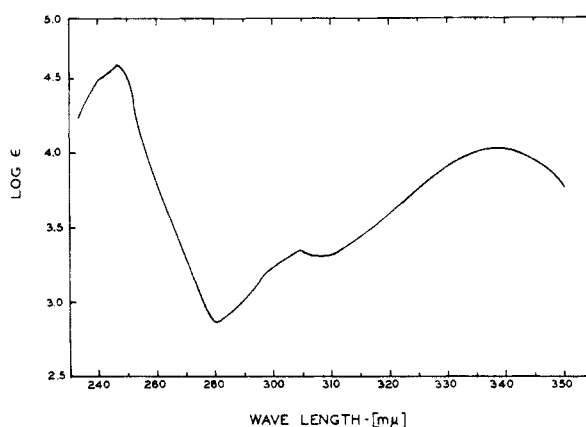


FIG. 2.—ULTRAVIOLET ABSORPTION SPECTRUM OF 9-*aci*-NITROFLUORENE IN ABSOLUTE ETHANOL.

from that of other 9-substituted fluorenes.⁶ A distinguishing element of the 9-*aci*-nitrofluorene spectrum is the relatively strong intensity of the $340\text{ m}\mu$ band as compared to that in fluorenone.

EXPERIMENTAL

Potassium 9-fluorenenitronate. This material was prepared in 68% yield by the method previously described.² At-

(6) Friedel and Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley and Sons, New York, N. Y., 1951, Spectra 329, 335 and 322, resp.

tempts were made to recrystallize the material without success. Partial oxidation occurred when it was heated in various solvents.

9-aci-Nitrofluorene. This material was prepared by acidification of a water solution of potassium 9-fluorenenitronate with either sulfuric acid or trifluoroacetic anhydride. It is precipitated immediately from water as a yellow-green powder, m.p. 134.5–137° (lit.², m.p. 134–137°).

aci-d-9-Nitrofluorene. A solution of 0.05 g. of potassium 9-fluorenenitronate in 2.2 g. of deuterium oxide was prepared in a flask protected from atmospheric moisture. The flask was immersed in an ice-bath and two drops of trifluoroacetic anhydride were added. The yellow-green *aci*-compound precipitated immediately. It was collected and stored in a vacuum desiccator over phosphorus pentoxide.

1,2-Dinitro-1,2-bidiphenyleneethane. This material was prepared by the method of Nenitzescu.⁷ It was recrystallized from acetic acid, m.p. 183–184° (lit.⁷ m.p. 184°).

Spectra. The infrared spectra were measured as Nujol mulls on a Perkin Elmer Model 21 infrared spectrophotometer with a rock salt prism. The ultraviolet spectrum was measured in absolute ethanol with a Beckman DK-1 ultraviolet spectrophotometer.

Acknowledgment. We are indebted to Dr. M. F. Hawthorne for the measurement of the ultraviolet spectrum and for aid in its interpretation, and to Dr. W. D. Emmons for helpful suggestions during the course of this study.

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(7) Nenitzescu, *Ber.*, **62**, 2669 (1929).

Catalytic N-Alkylation of Aniline with I-Propanol

B. B. CORSON AND H. DRESSLER

Received November 28, 1955

Rice and Kohn¹ recently reported that Raney nickel catalyzes the N-alkylation of aniline with alcohols but that U.O.P. nickel catalyst² is ineffective for this purpose. Evidently the batch of catalyst used by Rice and Kohn was poisoned or it was not properly reduced before use, as we have found the U.O.P. nickel catalyst to be at least as active as Raney nickel. An 80% yield of N-*n*-propylaniline was obtained in 6 hours whereas an equal amount of Raney nickel required 16 hours¹ to give the same yield.

Small amounts of acetaldehyde, propionaldehyde, and acetone were formed when ethanol, 1-propanol, and 2-propanol, respectively, were refluxed with U.O.P. nickel catalyst. This supports the reaction mechanism suggested by Rice and Kohn¹ for the catalytic N-alkylation of aniline with alcohols, namely that the alcohol is dehydrogenated to a carbonyl compound which then reacts with the amine to give an N-alkylideneamine (or an α -hydroxy-

amine) and that this intermediate is subsequently hydrogenated to the corresponding N-alkylaniline.

EXPERIMENTAL³

Materials. 1-Propanol, 2-propanol (both stored over Drierite), and aniline were freshly distilled. The U.O.P. nickel catalyst, obtained from the Harshaw Chemical Co., was prerduced at 425° in a stream of hydrogen, cooled under hydrogen, and pulverized under the appropriate alcohol before use.

N-n-Propylaniline. A mixture of 25 g. (0.28 mole) of aniline, 15 g. of prerduced U.O.P. nickel catalyst, and 80 g. (1.3 moles) of 1-propanol was refluxed with stirring for 6 hours. The cooled mixture was filtered and the catalyst was washed with 25 ml. of 1-propanol. The combined filtrate-wash was concentrated, and the residual liquid was distilled through a 10-cm. Vigreux column to give 29.3 g. (80% yield) of N-*n*-propylaniline, b.p. 110–111°/20 mm., n_D^{25} 1.5410.

The product was analyzed for secondary aromatic amine by electrometric titration.⁴

Anal. Calc'd for C₉H₁₃N: Secondary amine, 7.42 meq./g. Found: Secondary amine, 7.44 meq./g.

Its *phenylthiourea* derivative melted at 101–102°; its mixture melting point with an authentic sample was also 101–102°.⁵

Dehydrogenation of ethanol. A mixture of 79 g. of absolute ethanol and 15 g. of prerduced U.O.P. nickel catalyst was refluxed with stirring for 12 hours. The vapors which passed the water-cooled condenser were condensed in a Dry Ice-trap.

The condensate gave a *dimedone derivative* melting at 138–140° whose mixture melting point with an authentic sample of acetaldehyde dimedone derivative was also 138–140°.⁶

Dehydrogenation of 1-propanol. A mixture of 120 g. (2.0 moles) of 1-propanol and 10 g. of prerduced U.O.P. nickel catalyst was refluxed under a 30-cm. Vigreux column for 10 hours and 89 g. of distillate was collected.

Analysis of the distillate for carbonyl indicated the presence of 0.6 g. (0.01 mole) of propionaldehyde.

Anal. Calc'd for C₃H₆O: Carbonyl, 16.7 meq./g. Found: Carbonyl, 0.11 meq./g.

The distillate gave the *dimedone derivative of propionaldehyde*, m.p. 155–156°; its mixture m.p. with an authentic sample was also 155–156°.⁶

Dehydrogenation of 2-propanol. A mixture of 120 g. (2.0 moles) of 2-propanol and 10 g. of prerduced U.O.P. nickel catalyst was refluxed under a 30-cm. Vigreux column for 6 hours and 53.5 g. of distillate was collected.

Analysis of the distillate for carbonyl indicated the presence of 1.5 g. (0.03 mole) of acetone.

Anal. Calc'd for C₃H₆O: Carbonyl, 16.7 meq./g. Found: Carbonyl, 0.45 meq./g.

The distillate gave the *2,4-dinitrophenylhydrazone* of acetone, m.p. 122–123°; its mixture m.p. with an authentic sample was also 122–123°.⁶

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(3) All boiling points and melting points are uncorrected.

(4) Siggia, Hanna, and Kervenski, *Anal. Chem.*, **22**, 1295 (1950).

(5) Shriner and Fuson, *The Systematic Identification of Organic Compounds*, John Wiley and Sons, New York, 3rd ed., 1948.

(6) Huntress and Mulliken, *Identification of Pure Organic Compounds*, John Wiley and Sons, New York, 1941.

(1) Rice and Kohn, *J. Am. Chem. Soc.*, **77**, 4052 (1955).

(2) Ipatieff and Corson, *Ind. Eng. Chem.*, **30**, 1039 (1938).