Benzo Derivatives of Nitrocyclopentadiene

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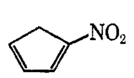
Received August 11, 1967

Protonation of the potassium salts of 1-nitroindene and 9-nitrofluorene in water solution occurs fastest at oxygen to yield in both cases the *aci* tautomers. In nonpolar solvents, *aci*-1-nitroindene tautomerizes to 3-nitroindene *via* 1-nitroindene; *aci*-9-nitrofluorene likewise tautomerizes to 9-nitrofluorene. The *aci* compounds do not tautomerize in hydroxylic solvents. On treatment with benzoyl chloride, both salts yield stable O-benzoyl derivatives.

Until recently, it was believed that the only tautomers produced by protonating salts of nitrocyclopentadiene,[1] and its annelated derivatives, 1-nitroindene[2] and 9-nitrofluorene,[3] were uniformly the *aci*-nitro compounds, produced by O protonation. Only in the case of 9-*aci*-nitrofluorene (I) has the *aci* structure been confirmed by spectral methods.[4] However, it has more recently been claimed, on the basis of bromination studies, that 9-*aci*-nitrofluorene (I) is the stable tautomer only in the crystal and in polar media; in nonpolar solvents it is transformed into 9-nitrofluorene (II).[3b]

I II

Because of the uncertainty of the information on the tautomeric forms of the above compounds, and inasmuch as *aci* tautomers are generally less stable thermodynamically than the corresponding nitro tautomers, we decided to reinvestigate these materials in order to establish the true nature of the species involved. Indeed, we have recently shown that the only simple product of protonation of the sodium salt of nitrocyclopentadiene was in fact 1-nitrocyclopentadiene[5] (III) rather than the *aci* compound reported by Thiele.[1]

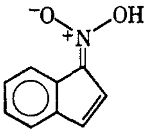


III

Results and Discussion

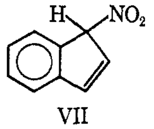
The potassium salts (IV and V) of 1-nitroindene and 9-nitrofluorene were prepared according to literature methods,[2,6] by treating the potassium salts of indene and fluorene with ethyl nitrate. The structures and spectra of these salts, and particularly their strong dependence on solvent, are reported elsewhere.[7]

Nitroindenes.—On acidifying an aqueous solution of IV, Wislicenus reported obtaining as a precipitate an unstable material, mp *ca.* 50°, to which he ascribed the *aci* structure, VI.[2] In agreement with his results, we also found that acidification of a cold aqueous solution of IV yielded a very fine, light yellow precipitate. However, collection of this material by filtration proved difficult owing to its fine particle size. In the time required to accomplish filtration, the material had turned dark orange; it darkened but did not melt on heating to 200°.



VI

Because of this instability of the protonated material,[2] no further attempts were made to isolate it; instead, the water solution was extracted with a suitable organic solvent immediately after acidification and the products were studied in solution. A chloroform-*d* solution of the product of acidification of IV, obtained in this manner and kept cold in a Dry Ice bath, was studied by nmr (see Table I). The spectrum showed a one-proton resonance at τ −0.9, one proton at 2.0, three protons at 2.5–2.8, and two protons at 3.3. This spectrum is uniquely consistent with the *aci* structure VI.[8] After the solution containing VI had stood at room temperature for 3 hr, the resonances of VI were largely replaced by new ones, at τ 2.4, 3.0, and 3.5 (Table I) which, by comparison with the recently reported spectrum of indene-1-carboxylic acid,[9] suggested that a considerable fraction of the VI had tautomerized to 1-nitroindene, VII.[10]



VII

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[1] J. Thiele, *Ber.*, **33**, 670 (1900).

[2] W. Wislicenus and K. Pfeilsticker, *Ann.*, **436**, 36 (1924).

[3] (a) C. D. Nenitzescu and C. D. Isacescu, *Ber.*, **63**, 2484 (1930); (b) C. D. Nenitzescu and I. G. Dinulescu, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1228 (1958), as translated in *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1185 (1958).

[4] J. P. Freeman and K. S. McCallum, *J. Org. Chem.*, **21**, 472 (1956).

[5] R. C. Kerber and M. J. Chick, *ibid.*, **32**, 1329 (1967).

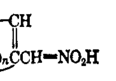
[6] W. Wislicenus and M. Waldmüller, *Ber.*, **41**, 3334 (1908).

[7] R. C. Kerber and A. Porter, *J. Amer. Chem. Soc.*, in press.

[8] Inasmuch as this appears to be the first reported nmr spectrum of an *aci*-nitro compound, it is worth noting that the resonance of the hydroxyl proton at τ −0.9 is similar to that of typical carboxylic acids in nonpolar media [*cf.* J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, p 91]. This suggests that *aci*-nitro compounds, like carboxylic acids, form hydrogen-bonded dimers in such media. Freeman and McCallum[4] previously proposed that I exists in such a dimeric form in the crystalline state.

[9] O. Meth-Cohn and S. Gronowitz, *Chem. Commun.*, 84 (1966).

[10] A referee has pointed out to us the work of H. B. Fraser and G. A. R. Kon [*J. Chem. Soc.*, 604, (1934)], who also reported obtaining unconjugated products of tautomerization, in their case from the *aci* compounds below.



$(CH_2)_n\overset{\overset{CH}{\|}}{C}CH{=}NO_2H$

$n = 3,4$

However, in these cases, the unconjugated tautomers were thermodynamically stable, probably owing to conformational effects. More recent studies in systems free of such effects have found only the conjugated isomers. See, for example, A. T. Nielsen, *J. Org. Chem.*, **27**, 2001 (1962), and H. Shechter and J. W. Shepherd, *J. Amer. Chem. Soc.*, **76**, 3617 (1954).

TABLE I

Compound	τ_1	τ_2	τ_3	τ_{4-6}	τ_7	J_{12}	J_{23}	J_{13}	Ref
Indene	7.01	3.87	3.34	*Ca.* 2.89	*Ca.* 2.89	2.02	5.58	1.98	*a*
syn-Indone oxime	...	3.55	*Ca.* 2.8	*Ca.* 2.8	1.75	...	6.0	...	*b*
anti-Indone oxime	...	3.17	3.02	*Ca.* 2.8	2.3	...	5.8	...	*b*
aci-1-Nitroindene (VI)	...	3.3	3.3	2.5–2.8	2.0	...	...	...	This work
XII	...	3.43	3.08	2.25–2.75	1.9	...	5.7	...	This work
1-Nitroindene (VII)	2.4	3.5	3.0	2.5–2.8	2.5–2.8	2.0	5.8	2.0	This work
3-Nitroindene (VIII)	6.40	2.45	...	2.55–2.85	(τ_4) 1.95	1.9	...	...	This work
Indene-1-carboxylic acid	5.47	3.57	3.24	*Ca.* 2.76	2.45	1.9	5.7	1.9	*c*
Methyl indene-3-carboxylate	6.57	2.67	...	...	(τ_4) 1.97	2	...	...	*d*

[a] D. D. Elleman and S. L. Manatt, *J. Chem. Phys.*, **36**, 234 (1962). [b] Personal communication from Dr. Sylvan E. Forman, FMC Corp; *cf. J. Org. Chem.*, **29**, 3323 (1964); the configuration assignments are our own, based on data in G. Karabatsos, R. A. Taller, and F. M. Vane, *J. Amer. Chem. Soc.*, **85**, 2326 (1963). [c] See ref 9. [d] A. Melera, M. Claesen, and H. Vanderhaeghe, *J. Org. Chem.*, **29**, 3705 (1964).

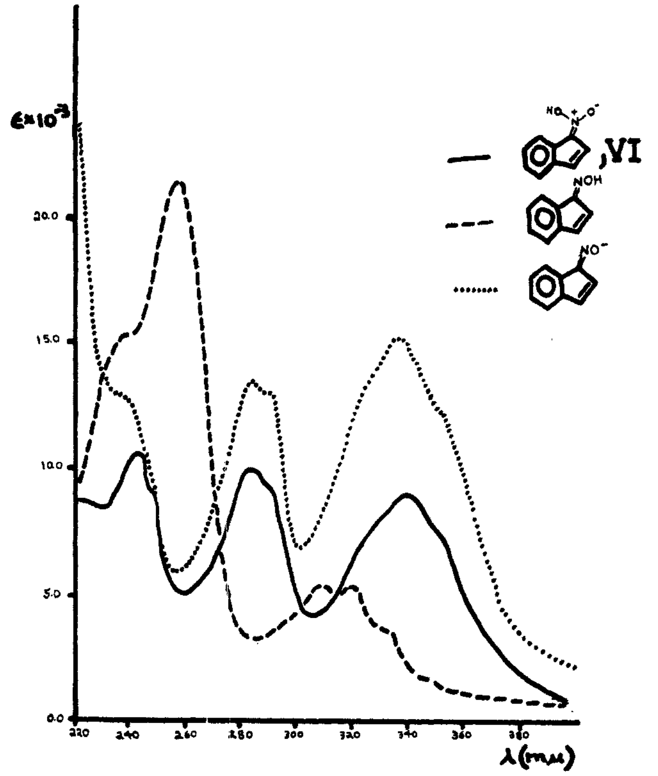
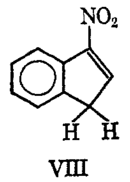


Figure 1.—Ultraviolet spectra of 1-*aci*-nitroindene and indone oxime.

The nmr spectrum of the 3-hr-old sample also showed a doublet at τ 6.40, which continued to increase with time, even as the resonances of VI and VII decreased. After 18 hr a steady state had been reached; the spectrum contained a two-proton doublet at τ 6.40 (J = 1.9 cps), a one-proton multiplet at 1.95, a one-proton triplet at 2.45, (J = 1.9 cps), and a three-proton multiplet at τ 2.55–2.85. These data showed that the ultimate product was 3-nitroindene, VIII.



VIII

The sequence of changes observed in the nmr spectra demonstrates that the rates of protonation at the various positions of the IV anion decrease in the order O > C-1 > C-3[11] and that at equilibrium in nonpolar solution the only isomer detectable by nmr is 3-nitroindene, VIII.

Although the facile interconversion of the nitroindene tautomers makes unambiguous interpretation of other spectra difficult, their origin can usually be inferred from internal evidence. Thus, the same ultraviolet spectrum (Figure 1), due to VI, was obtained either by acidifying an ethanol solution of the salt IV and measuring the spectrum directly or by acidifying an aqueous solution, extracting rapidly with ether, and measuring the spectrum of the diluted ether extract. The attribution to VI is supported by the similarity of the spectrum to that of IV[7] (save for shifts of the maxima to shorter wavelengths) and to that of indone oxime, particularly in basic solution (Figure 1).[12]

As the ether solution of VI stood at room temperature, this spectrum slowly decayed (half-life about 3 hr). After 27 hr, the spectrum showed only broad maxima at 238 and 289 mμ (ε *ca.* 7000 and 3000, respectively), which are presumably due to 3-nitroindene, IX. By comparison, indene absorbs at 252 mμ (ε 9900) in isooctane;[13] 2-nitro-2-butene absorbs at 235 mμ (ε 6100) in hexane.[14]

The infrared spectra of solutions of VI, prepared by extracting a freshly acidified solution of IV with carbon tetrachloride or chloroform, showed O–H absorption as a very broad band between 3600 and 2200 cm^{-1} and C=N at 1654 cm^{-1}.[15] Strong bands not attributable to the hydrocarbon portions of the molecule also appeared at 1253 and 957 cm^{-1}. Similar bands appear in the infrared spectrum of I; these may prove to be characteristic of the *aci*-nitro grouping, $R_2C=NO_2H$.

On standing in carbon tetrachloride at room temperature, this spectrum slowly disappeared. After 20 hr,

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(11) This assumes that tautomerization in $CDCl_3$ occurs *via* the IV anion; it is presumably catalyzed by small amounts of water present because of the extraction procedure.

(12) The spectra of indone oxime were graciously supplied to us by Dr. Sylvan Forman of F.M.C. Corp. to whom we are very grateful; *cf. J. Org. Chem.*, **29**, 3323 (1964).

(13) A. P. I. Research Project No. 44, I, 321 (1949); *cf.* "Organic Electronic Spectral Data," Vol. 1, M. J. Kamlet, Ed., Interscience Publishers Inc., New York, N. Y., 1960, p 243.

(14) E. A. Braude, E. R. H. Jones, and G. G. Rose, *J. Chem. Soc.*, 1104 (1947).

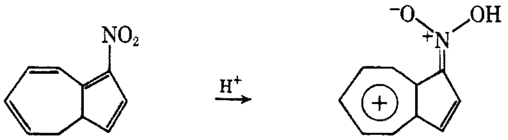
(15) C=N stretching frequencies of other *aci*-nitro compounds fall in the region 1630–1684 cm^{-1}; *cf.* S. S. Novikov, *et al.*, Proceedings of the International Symposium on Nitro Compounds, Warsaw, 1963, T. Urbanski, Ed., MacMillan and Co., Inc., New York, N. Y., 1964, p 119. This paper disputes the existence of covalent *aci* structures, a viewpoint which is inconsistent with the spectra reported herein.

the spectrum showed two strong bands at 1550 and 1359 cm^{-1} due to the nitro group of IX and a medium band at 1460 cm^{-1} due to the CH$_2$ group.

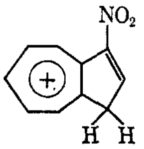
The spectra reported here confirm Wislicenus' conclusion that *aci*-1-nitroindene (VI) is the kinetically controlled product of protonation of IV. However, in nonpolar solvents VI tautomerizes cleanly to 3-nitroindene, IX. None of the other isomers can be detected at equilibrium in these nonpolar solvents.

In contrast to these results, solutions of VI in methanol or ethanol showed no substantial change in ultraviolet-visible absorption on standing at room temperature for several hours. Thus it appears that the tautomeric equilibrium among the nitroindenes is solvent sensitive: *aci*-1-nitroindene (VI) is favored in hydroxylic solvents; 3-nitroindene (IX) is favored in nonpolar solvents.

The thermodynamic preference for *aci* compound VI in hydroxylic media is consistent with the results of Meuche and Heilbronner,[16] who have reported that protonation of 1-nitroazulene in trifluoroacetic–sulfuric acid gave only the *aci* compound X which is isoelectronic with VI. No 3-nitroazulenium ion could be detected by nmr.



X



Nitrofluorene.—Acidification of an aqueous solution of the potassium salt of 9-nitrofluorene (V) produces a light yellow precipitate, which can be collected and dried. This material has been shown to be 9-*aci*-nitrofluorene, I, by both chemical[3] and spectral[4] methods. We report here only those features of the spectra which support our findings in the nitroindene series and which bear upon the question of tautomerism of nitrofluorene.

Dissolution of I in ethanol gives a solution whose electronic spectrum is that of the salt V. In order to obtain a spectrum of I, 1 drop of mineral acid must be added to prevent ionization of I, which is evidently a strong acid in ethanol.[17] The *aci* compound, I, is relatively stable in acidic ethanol; the long wavelength peaks do not change in shape or intensity over a period of at least 1 day.

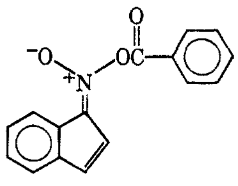
However, in ether or tetrahydrofuran (THF) solution, the spectrum of I is not stable. The long wavelength peaks decay at room temperature leaving maxima at 245, 253, and *ca.* 271 mμ (broad shoulder). The nmr spectrum in THF also behaved in a manner suggesting tautomerism of I to II. The OH resonance of a freshly dissolved sample of slightly wet I appeared at τ 2.1; as the material stood at room temperature, the OH resonance moved upfield toward the free water value, τ 5.0. Simultaneously, the aromatic pattern changed from that of II, which showed three complex multiplets centered at τ 1.85, 2.30, and 2.70 (relative areas 1:1:2) to a single broad multiplet at τ 2.2–3.1.

We interpret the changes in these spectra as being due to tautomerism of I to II in THF,[18] in agreement with Nenitzescu's findings.[3b]

Benzoyl Derivatives.—On treatment with benzoyl chloride, alcohol solutions of IV or V rapidly precipitate bright yellow benzoyl derivatives. In the case of V the product has been shown by chemical means to be O-benzoyl-9-*aci*-nitrofluorene, XI.[19] This is consistent with our observation that the ultraviolet spectra of I and of the benzoyl derivative are nearly superimposable.

The benzoyl derivative of IV was prepared by Wislicenus[2] and assigned the structure 1-benzoyl-3-nitroindene, in part because it was alleged to be soluble in base. We have found, however, that the material is not soluble in 10% aqueous potassium hydroxide; it dissolves in Claisen's alkali to give a solution whose ultraviolet spectrum is that of the salt IV. The ultraviolet spectrum of the benzoyl derivative itself is nearly identical with that of 1-*aci*-nitroindene, VI. The infrared spectrum shows C=O and C=N bonds at 1764 and 1600 cm^{-1}, compared with 1754 and 1616 cm^{-1} for XI. Lastly, the nmr spectrum of the benzoyl derivative (Table I) shows the presence of an unsubstituted double bond in the five-membered ring.

These data show unequivocally that the benzoyl derivative of IV has the structure O-benzoyl-1-*aci*-nitroindene, XII, analogous to that of XI.[20]



XII

Since the O-benzoyl derivatives were obtained in good yield from both IV and V, it is clear that kinetically controlled acylation, like protonation, occurs far faster at oxygen than at any other position of IV or V. It seems probable that other reactions of these anions with electrophiles will also occur preferentially at oxygen, although thermodynamic control may in some cases favor other positions.

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer Infracord, Model 137B, calibrated with a polystyrene film. Ultraviolet-visible spectra were obtained on a Perkin-Elmer Model 202 spectrophotometer. Proton magnetic resonance spectra were obtained on a Varian A-60 spectrometer; chemical shifts are reported as τ values relative to tetramethylsilane as internal

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[16] D. Meuche and E. Heilbronner, *Helv. Chim. Acta*, **45**, 1565 (1962).

[17] The published spectrum[4] is at least partly that of the anion.

[18] The 9 proton of II was not observed directly in the nmr spectrum, perhaps being buried among the complex aromatic pattern. The aliphatic proton of diphenylnitromethane falls at τ 3.15; that of II should fall at still lower field.

[19] (a) C. D. Nenitzescu and D. A. Isacescu, *Bull. Soc. Chim. Romania*, **14**, 53 (1932); *cf. Chem. Abstr.*, **27**, 964 (1934); (b) E. H. White and W. J. Considine, *J. Org. Chem.*, **22**, 1745 (1957).

[20] This possibility was first suggested in ref 19b, footnote 4.

standard (τ 10.00). Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Potassium Salt (IV) of 1-Nitroindene.[2]—Potassium metal (10.0 g, 0.26 g-atom) was added in small portions to a mixture of 40 ml of absolute ethanol and 30 ml of absolute ether in a three-neck flask fitted with nitrogen inlet tube, mechanical stirrer, and dropping funnel. The mixture was stirred under a nitrogen atmosphere until all of the metal dissolved, then a mixture of 25 g (0.22 mol) of freshly distilled indene and 25 g (0.24 mol) of ethyl nitrate in 100 ml of absolute ether was added over a 2-hr period. The temperature was kept within the range 10–30° by use of an ice bath. The mixture was stirred an additional 45 min. Ether was added as necessary to keep the mixture stirable as a voluminous deep yellow precipitate formed. The precipitate was collected by filtration and the solid, which darkened rapidly on exposure to air while wet, was dried in a vacuum desiccator over KOH. The yield was 23.2 g (53%).

The crude salt was purified by dissolving it in 20 ml of acetone, bubbling carbon dioxide through the black solution for 15 min, adding charcoal, and filtering the solution. The precipitate was washed with acetone to give a total of about 50 ml of acetone solution. About 500 ml of chloroform was then added to reprecipitate the salt, as a yellow solid, which was redried *in vacuo*. The product darkened on heating to 200°, but did not melt below 340°. Spectral data appear elsewhere.[7]

The Potassium Salt (V) of 9-Nitrofluorene.[6,21]—V was made in the same manner as IV, using 5.85 g (0.15 g-atom) of potassium, 25.0 g (0.15 mol) of fluorene, and 13.7 g (0.15 mol) of ethyl nitrate. The mixture was filtered after 15 hr, giving the salt as a light yellow powder, in 68% yield. Spectral data appear elsewhere.[7]

Attempted Isolation of Nitroindene.—About 1.0 g of salt IV was dissolved in water and the cold solution was acidified with cold 3% HCl until no further precipitate (a light yellow solid) appeared. Filtration proved slow because of the fine particle size of the precipitate, but eventually resulted in a sticky, dark orange solid, which darkened but did not melt on heating to 200°. No further work was done with this material; rather, the nitroindenes were studied in solution.

***aci*-1-Nitroindene (VI) and 3-Nitroindene (VIII).**—Salt IV was dissolved in water and an equal volume of an immiscible organic solvent was added. The mixture was cooled to 0° and then acidified with cold 3% HCl. The layers were mixed, the organic layer was quickly removed by pipet, and the spectrum was taken. Solvents used included carbon tetrachloride (for ir), chloroform-*d* (for ir and nmr), and ether (for uv).

The ultraviolet spectrum attributed to VI could be obtained either by the above procedure or by acidifying an ethanol solution of IV and measuring the spectrum directly. In ethanol, the spectrum showed peaks at 240 mμ (ϵ 11,100), 248 (shoulder, 9000), 282 (10,000), *ca.* 290 (shoulder, 9200), *ca.* 325 (shoulder, 7800), 338 (9200), and *ca.* 354 (shoulder, 6900). In ether, this spectrum decayed with a half-life of about 3 hr at room temperature; after 2 days the spectrum showed only two peaks at 238 mμ (ϵ *ca.* 7000) and 289 mμ (ϵ *ca.* 3000). In ethanol no substantial change in the ultraviolet spectrum of VI occurred during several hours. Over longer periods, decomposition occurred; no evidence of tautomerism to VIII or VII was found in ethanol solution.

The infrared spectrum of VI showed bands at 3600–2200 (s, broad), 1550 m, 1515 w, 1460 m, 1370 m, 1325 m, 1253 s, and 957 cm^{-1} m. As the sample stood at room temperature these bands disappeared slowly. After 20 hr, the spectrum showed bands at 1603 w, 1553 s, 1481 w, 1460 m, 1439 w, and 1359 cm^{-1} s.[21]

The nmr spectra of VI, VIII, and VII are given in Table I. The solution of VI in chloroform-*d* was kept at −78° between its preparation and obtaining the initial nmr spectrum.

9-*aci*-Nitrofluorene (I) and 9-Nitrofluorene (II).[21]—Compound I was prepared in small quantities as needed by acidification of water solutions of V with dilute hydrochloric or sulfuric acids. It was collected by filtration and dried for up to 1 day *in vacuo* over KOH. The material was a cream solid; typical mp 116–118° (lit.[4] mp 134.5–137°). The only impurity detected by spectral methods was water.[22]

The ultraviolet spectrum of I dissolved in 95% ethanol was identical with that of V.[7] Addition of 1 drop of sulfuric acid to this solution or to a solution made by dissolving V in 95% ethanol gave the spectrum of I, which showed bands at *ca.* 231 mμ (shoulder, ϵ 6200), 236 (6900), 256 (3700), 266 (3600), *ca.* 294 (1700), *ca.* 327 (shoulder, 2100), and 338 (2400). This spectrum persisted with little or no change for at least 18 hr. The same spectrum could be obtained directly by dissolving I in THF or ether; however, the spectrum slowly changed over the course of several hours to one showing maxima at 245, 253, and 271 mμ (broad shoulder). Addition of base after 25 hr did not regenerate the anion VI, showing irreversible changes after tautomerism.[3b]

The infrared spectrum of I as a Nujol mull was similar to that reported,[4] but with fewer small bands in the fingerprint region. I was insufficiently soluble in nonpolar solvents to give usable solution spectra.

The nmr spectrum of I freshly dissolved in THF showed three multiplets centered at τ 1.85, 2.30, and 2.70, relative areas about 1:1:2, due to the aromatic protons, and a somewhat broadened singlet at τ 2.1. After the sample had stood at room temperature for 24 hr, the O–H resonance had moved upfield to τ 3.1; after 3 more days, it had reached τ 4.2 and the aromatic pattern was largely collapsed to a single broad multiplet from τ 2.2 to 3.1. Addition of 1 drop of water moved the O–H resonance to τ 5.0 and raised its intensity.

O-Benzoyl-1-*aci*-nitroindene (XII).—A solution of benzoyl chloride (2.50 g, 0.018 mol) in ether was added slowly to a cooled solution of 3.00 g of the salt IV (0.015 mol) in 20 ml of methanol. Fine orange crystals precipitated almost at once. Filtering, washing with water, and drying gave 3.97 g of XII (78% crude yield). Recrystallization from benzene gave material of mp 118–119.5° dec (lit.[2] mp 121° dec[23]).

Anal. Calcd for $C_{16}H_{11}NO_3$: C, 72.07; H, 4.15; N, 5.21. Found: C, 72.16; H, 4.18; N, 5.07.

Compound XII was insoluble in 10% aqueous KOH, but soluble in Claisen's potash. Dilution of this solution with methanol gave a solution whose ultraviolet spectrum was that of the salt IV. Compound XII itself in hexane gave an ultraviolet spectrum very similar to that of VI: λ_{max} 238 mμ (ϵ 15,200), *ca.* 275 (shoulder, 9600), 283 (10,900), *ca.* 292 (shoulder, 9400), *ca.* 325 (shoulder, 7800), 336 (9500), and 351 (shoulder, 6600).

The infrared spectrum of XII as a Nujol mull showed bands at 1764 m, 1600 s, 1447 m, 1370 w, 1346 m, 990 m, broad, 813 m, 752 m, and 699 cm^{-1} m. The nmr spectrum in acetone is described in Table I.

O-Benzoyl-9-*aci*-nitrofluorene (XI).[21]—XI was prepared in the same manner as XII, in 75% yield. Recrystallization from hexane–benzene brought the melting point to 126.5–127.5° (lit.[19b] mp 134–135° [23]).

Anal. Calcd for $C_{20}H_{13}NO_3$: C, 76.20; H, 4.13; N, 4.45. Found: C, 76.40; H, 4.35; N, 4.70.

The ultraviolet spectrum of XI in ethanol was similar to that of I, showing maxima at 231, 254, 263, 321, and 336 mμ with essentially the same intensity relationships as I. Dilution of a solution of XI in Claisen's potash with methanol gave the ultraviolet spectrum of salt V. The infrared spectrum of XI as a Nujol mull showed bands at 1754 s, 1616 s, 1590 sh, 1399 s, 1081 m, 1000 m, 954 m, 775 s, 732 s, and 697 cm^{-1} s. The nmr spectrum showed two groups of aromatic protons, centered at τ 1.78 and 2.5 in about a 1:4 ratio.

Registry No.—I, 15206-29-8; II, 14544-96-8; III, 10236-21-2; IV, 15153-27-2; VI, 15095-56-4; VII, 15095-57-5; VIII, 15095-58-6; XI, 15095-51-9; XII, 15095-59-7.

Acknowledgments.—This work was supported in part by a F. G. Cottrell Grant from the Research Corp. We wish to thank Mr. Albert Porter for performing some of the experiments in the nitrofluorene series.

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(21) This experiment was performed by Mr. Albert Porter.

(22) A sample dried for only 10 min after filtration gave a higher melting point, 125–128°. A comparison of our ir spectra (*vide infra*) with that of Freeman and McCallum[4] shows our materials to be the same, save that the O–H band of our material (*ca.* 3500–2500 cm^{-1}) is at higher frequency than theirs (*ca.* 3000–2000 cm^{-1}). Conceivably their higher melting material is a hydrate of I.

(23) The melting point of this compound is strongly dependent on the rate of heating and is not therefore a reliable physical constant.