minutes at which time the evolution of gas had ceased. The product was taken up in ether, washed with sodium bicarbonate solution and dried with magnesium sulfate. The ether was distilled and the liquid residue was chromatographed on 100 g. of activity I alumina as described above. There was obtained 0.199 g. (8.8%) of 3,6-epoxycycloheptanecarbonitrile, m.p. 102.8–103.6°, and 1.37 g. (60%) of 3,6-epoxycycloheptanecarbonitrile, m.p. 87–88°.

Decarboxylation of 1-Cyano-3,6-epoxycycloheptanecarboxylic Acid, m.p. 214.5–216.6° dec., in Quinoline.—Treatment of 2.50 g. of 1-cyano-3,6-epoxycycloheptanecarboxylic acid, m.p. 214–217° dec., as described above for the isomeric acid X or XI with m.p. 177.2–178.6° dec. afforded 0.963 g. (53%) of 3,6-epoxycycloheptanecarbonitrile, m.p. 102.8–103.6°, and 0.168 g. (9.2%) of 3,6-epoxycycloheptanecarbonitrile, m.p. 87–88°.

Thermal Decarboxylation of 1-Cyano-3,6-epoxycycloheptanecarboxylic Acid, m.p. 214.5–216.6° dec.—1-Cyano-3,6-epoxycycloheptanecarboxylic acid, m.p. 214–217° dec., 2.00 g., was heated at 240° until the evolution of gas had ceased (approximately 20 minutes). The product was isolated in the manner described above and afforded 0.353 g. (23%) of 3,6-epoxycycloheptanecarbonitrile, m.p. 102.6–103.8°, and 0.467 g. (31%) of 3,6-epoxycycloheptanecarbonitrile, m.p. 87–88°.

Quantitative Infrared Analysis of the Nitrile Mixtures.—Mixtures of the nitriles XIII and XIV obtained by heating the acids X or XI either alone or in quinoline were purified as described above, but subjected to infrared analysis rather than chromatography on alumina. The spectra were determined at concentrations of 100 mg./ml. in carbon tetrachloride solution. The same sample and blank cells were used for each determination and the 0 and 100% transmission lines were determined for each of the pure nitriles. The compositions of the mixtures were estimated from these curves in the usual manner, using the percentage transmission at 11.22 μ of the nitrile with m.p. 102.8–103.6° and the percentage transmission at 11.43 μ of the nitrile with m.p. 87.0–88.0° in the calculations. The normalized results and the unnormalized total yields are recorded in Table I.

Thermal Stability of 3,6-Epoxycycloheptanecarbonitrile (XIII and XIV).—A sample of the pure isomeric nitrile with m.p. 87–88° was heated in an oil-bath at 235 ± 5° for 30 minutes. The sample was cooled and its infrared spectrum determined at a concentration of 100 mg./ml. in carbon tetrachloride. The spectrum was identical with that of the starting material. A sample of the nitrile with m.p. 102.8–103.6° also showed no change when treated as described above. Heating both of the nitriles in this manner with an equal weight of adipic acid resulted in no change in the spectrum of the nitrile with m.p. 87.0–88.0°, and while the spectrum of the product recovered from the nitrile with m.p. 102.8–103.6° was changed, it did not show absorption peaks characteristic of the lower-melting isomer.

Stability of 3,6-Epoxycycloheptanecarbonitriles (XIII and XIV) in Quinoline at 200°.—A sample, 0.109 g., of 3,6-epoxycycloheptanecarbonitrile, m.p. 102.5–103.5°, was dissolved in 1.0 ml. of quinoline and heated in an oil-bath at 200° for 1 hour. The solution was cooled and poured into excess, iced, dilute sulfuric acid and the acidic solution was extracted with four 25-ml. portions of ether. The ether extracts were dried with potassium carbonate and the ether was distilled. The infrared spectrum of the product obtained, 0.105 g., was identical with the spectrum of the original nitrile.

Similar treatment of 0.100 g. of 3,6-epoxycycloheptanecarbonitrile, m.p. 87–88°, afforded 0.100 g. of recovered material which was identical, according to the infrared spectrum, with the starting material. Similar treatment of both nitriles mixed with an equal weight of adipic acid resulted in no change in the spectrum of either isomer.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

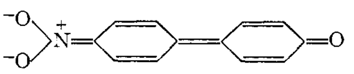
Conjugation in the Naphthalene System. I. Acidity of Nitronaphthols

BY KURT C. SCHREIBER AND SR. MARY CLAIRE KENNEDY, S.S.J.

RECEIVED JULY 28, 1955

The dissociation constants of 4-, 5- and 6-nitro-1-naphthol, 3-phenanthrol and 9-nitro-3-phenanthrol have been measured in 48% aqueous ethanol. The data are interpreted as indicating a lack of significant contribution by resonance structures involving conjugation between the two rings making up the naphthalene system to the electronic structures of the ground states of the conjugate base of these compounds.

In a recent paper[1] it was shown that a nitro group in the 4′-position of a biphenyl system enhances the acidity of 4-hydroxybiphenyl only inductively and that, therefore, resonance structure I contributes little toward the stabilization of the anion.



I

These results have focused attention upon the naphthalene system where a similar situation is present when the two functional groups are attached in the 1,5-positions, respectively.

Methods and Results

Materials.—**4-Nitro-1-naphthol** was prepared according to the method of Hodgson and Kilner,[2] but in the separation of the 2-isomer the method of Fourneau[3] proved more useful.

5-Nitro-1-naphthol.—5-Nitro-1-naphthylamine was diazotized by the inverse addition method of Hodgson and Walker[4] and converted to the naphthol by the procedure of Kaufler and Bauer.[5]

6-Nitro-1-naphthol.—This compound was prepared according to the procedure of Hodgson and Turner[6] except for the reductive decomposition of the 6-nitro-2-diazo-1-naphthol, which was carried out with alkaline sodium hydrosulfite in ethanol.

3-Phenanthrol and 9-nitro-3-phenanthrol were prepared by the methods of Fieser[7] and Burger,[8] respectively.

Dissociation Constants.—The data required for the calculation of the apparent pK_a using the Henderson–Hasselbalch equation were obtained (a) potentiometrically and (b) spectrophotometrically. Potentiometric titrations of the compounds in 48% ethanol with 48% aq. ethanolic sodium hydroxide solutions (0.03 to 0.06 N) were made with the aid of a Beckman Model G pH meter using glass and calomel electrodes. The pK_a's were determined from the half neutralization point on the titration curve. No sodium ion corrections for the glass electrode at high pH's were made, since it was found that using Nomograph 22N of Beckman Bulle-

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[1] V. P. Kreiter, Wm. A. Bonner and R. H. Eastman, THIS JOURNAL, **76**, 5770 (1954).

[2] H. H. Hodgson and E. Kilner, *J. Chem. Soc.*, **125**, 807 (1924).

[3] E. Fourneau and Balaceano, *Bull. soc. chim. France*, **37**, 1602 (1925).

[4] H. H. Hodgson and J. Walker, *J. Chem. Soc.*, 1620 (1933).

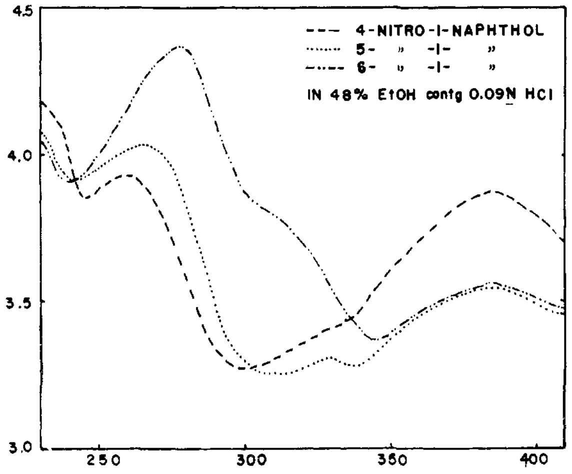
[5] F. Kaufler and E. Bauer, *Ber.*, **40**, 3269 (1907).

[6] H. H. Hodgson and H. S. Turner, *J. Chem. Soc.*, 8 (1944).

[7] L. Fieser, THIS JOURNAL, **51**, 2460 (1929).

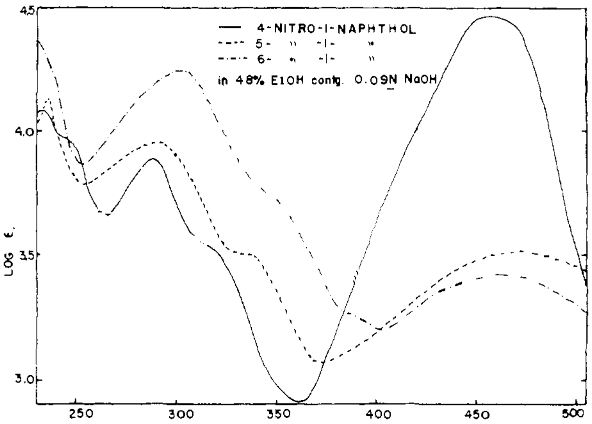
[8] A. Burger and E. Mosettig, *ibid.*, **56**, 1745 (1934).

tin 225-A, the variation in the pK_a under the conditions used for the titrations would be within the experimental error.



Wave length, mμ.

Fig. 1.—Ultraviolet absorption spectra.



Wave length, mμ.

Fig. 2.—Ultraviolet absorption spectra.

The procedure for obtaining the pK_a's from spectrophotometric data has been described by Kreiter, *et al.*,[1] and was followed in this work. The spectra of the various compounds in 48% aq. ethanol containing either hydrogen chloride (0.09 *N*) or sodium hydroxide (0.09 *N*) are shown in Figs. 1 and 2, respectively, and the peaks used in the calculations are listed in Table I. The results obtained are collected in Table II. The pK_a's of phenol as well as of nitrophenols were also determined in order to be able to compare them with the nitronaphthols in the same solvent system.

TABLE I

WAVE LENGTHS AND MOLAR EXTINCTION COEFFICIENTS AT ABSORPTION MAXIMA USED FOR CALCULATION OF DISSOCIATION CONSTANTS AT 25°

Compound	Acid form λ_{max}	Acid form $\epsilon \times 10^{-3}$	Conjugate base form λ_{max}	Conjugate base form $\epsilon \times 10^{-3}$
4-Nitro-1-naphthol (II)	260	8.37	288	7.74
5-Nitro-1-naphthol (V)	264	10.6	290	9.03
6-Nitro-1-naphthol (IX)	278	23.8	303	17.6
1-Naphthol	295	5.36	333	2.35
Phenol	271	1.96	239	9.32

TABLE II

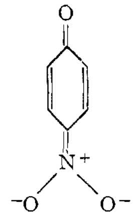
DISSOCIATION CONSTANTS IN 48% AQUEOUS ETHANOL AT 25°

Compound	pK_a Spectrophotometric	pK_a Potentiometric
Phenol	10.92	...
p-Nitrophenol[a] (III)	...	7.81
m-Nitrophenol (VIII)	...	9.25
1-Naphthol	10.69	10.65[c]
4-Nitro-1-naphthol[b] (II)	...	6.36
5-Nitro-1-naphthol (V)	9.20	9.25
6-Nitro-1-naphthol (IX)	9.61	9.60
3-Phenanthrol	...	10.63[c]
9-Nitro-3-phenanthrol (X)	...	9.08

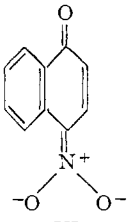
[a] The value given by H. Schwarzenbach (*Helv. Chim. Acta*, 22, 360 (1939)) in 49.9% ethanol is 7.68. [b] R. Arnold and J. Sprung (*J. Am. Chem. Soc.*, 61, 2475 (1939)) report a value of 6.60 at 30° under similar conditions. It is not clear whether the per cent. ethanol is the same. [c] These values were obtained by measuring the *p*H of a solution exactly half-neutralized.

Discussion

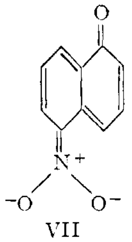
A comparison of the pK_a values of 4-nitro-1-naphthol (II) and of 1-naphthol shows that the nitro substituent in the 4-position increases the acidity of the parent compound by a factor of 22,000, while a nitro group in the 5-position of the naphthalene ring system enhances the acidity only by a factor of 25. The behavior of II parallels that of *p*-nitrophenol (III), a compound which is approximately 650-fold more acidic than phenol. In III the increase in acidity has been ascribed to the additional resonance stabilization of the anion by the oxygen of the nitro group, as illustrated by structure IV. Resonance structures in which the oxygen of the nitro group is bearing the negative charge of the anion can be written for the anion of both II and of 5-nitro-1-naphthol (V). These are shown in VI and VII, respectively. On the other hand, no such resonance structures can be written for either *m*-nitrophenol (VIII) or 6-nitro-1-naphthol (IX). However, looking at Table II, it is observed that both VIII and IX are more acidic than their respective parent compounds. This increase is due to the powerful inductive effect[9] of the nitro group. Since the difference between V and IX is only 0.35 pK_a unit, the conclusion must be drawn that the contribution of structure VII to the ground state of V anion can be only of secondary importance.



IV



VI



VII

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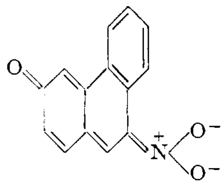
(9) G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 172.

The conclusion of the last paragraph, that the nitro group in the 5-position of the naphthalene ring system is acting only inductively, makes it necessary to search for the reason why resonance structure VI is more effective than VII in stabilizing the anions. On close examination it will be noted that in structure VI one ring of the naphthalene system is quinoid while the other is still benzenoid. In VII, however, both rings are quinoid. This means that VII represents a structure of higher energy than VI and therefore its contribution to the resonance hybrid is considerably smaller. Eastman[1] advanced a similar explanation for the absence of enhanced acidity in 4′-nitro-4-hydroxybiphenyl.

The observation that the nitro group in the 4-position of 1-naphthol is about 30 times more acidifying than the same group in the *para* position of phenol can be explained by considering the difference in the ease of formation of a *para*-quinoid system between benzene and naphthalene. The formation of the *para*-quinoid form is energetically more favorable in II than in III, and, therefore, structure VI contributes more to the resonance hybrid of the II anion than resonance structure IV to the hybrid of III anion.

Included in Table II are also data for 3-phenanthrol and 9-nitro-3-phenanthrol (X). The latter compound is another representative of the class of compounds in which the two functional groups are attached to different rings of a fused ring system. Again in X as in V it is possible to write a resonance structure for the anion, shown in XI, where the negative charge can be stabilized by the oxygen of the nitro group. The experimental data indicate that this system is similar to V, in which there is little resonance interaction between the nitro and the hydroxy group.



XI

Summarizing, it has been shown that the nitro group in the 4-position of 1-naphthol is more acidifying than in the *para* position of phenol, while a nitro group in the 5-position of 1-naphthol acts essentially only inductively.

Acknowledgment.—The authors wish to thank the National Science Foundation for financial support of this research project.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA]

Mechanisms for the Formation of Naphthylpiperidines from Naphthyl Bromides[1]

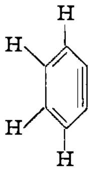
BY J. F. BUNNETT AND T. K. BROTHERTON[2]

RECEIVED JUNE 24, 1955

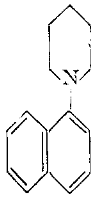
Both α- and β-bromonaphthalene react with piperidine at 230° to form the corresponding N-naphthylpiperidine. However, each bromonaphthalene reacts with sodium amide and refluxing piperidine to form a mixture of the two naphthylpiperidines (II and III). The latter reactions presumably involve the "benzyne" type of mechanism, and the former definitely do not.

For some time it has been recognized that unactivated aryl halides, such as tolyl and unsubstituted phenyl and naphthyl halides, differ from activated aryl halides, such as *o*- and *p*-nitrophenyl halides, in their mode of reaction with nucleophilic reagents. The difference is more profound than mere dependence of reaction rate on the presence or absence of activating groups. It is most evident in the orders of replaceability of the four halogens: in activated aryl halides, the order is F $>>$ Cl $\sim$ Br $\sim$ I, while in unactivated phenyl halides the order is I $>$ Br $>$ Cl $>$ F, as in alkyl halides.[3,3a]

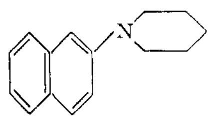
One of the reactions of unactivated aryl halides formerly regarded as a straightforward replacement is now recognized to involve a special and unique mechanism. This is the reaction with alkali metal amides to form amines; for example, the reaction of chlorobenzene with potassium amide to form aniline. Roberts and co-workers[5] have presented evidence that in this reaction the elements of hydrogen chloride are split out to form a symmetrical intermediate resembling "benzyne" (I), and that this intermediate then adds ammonia to form aniline. The formation of rearranged products from substituted phenyl halides, such as *m*-anisidine from *o*-iodoanisole and sodium amide,[6] is explicable in terms of this mechanism.



I



II



III

In the reactions of phenyl and naphthyl halides

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[1] Presented to the XIVth International Congress of Pure and Applied Chemistry, Zurich, July, 1955.

[2] American Enka Fellow, 1954–1955.

[3] J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 333 (1951).

[3a] The order of replaceability from activated halides depends somewhat on the nucleophilic reagent.[4]

[4] G. S. Hammond and L. R. Parks, THIS JOURNAL, **77**, 340 (1955).

[5] J. D. Roberts, H. E. Simmons, L. A. Carlsmith and C. W. Vaughan, *ibid.*, **75**, 3290 (1953); J. D. Roberts, private communications.

[6] H. Gilman and S. Avakian, THIS JOURNAL, **67**, 349 (1945).