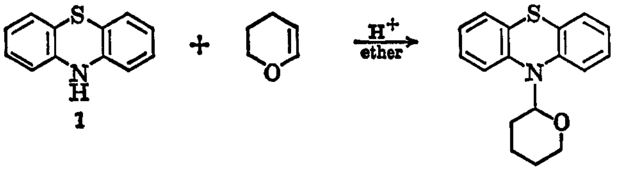
TABLE I

N-(2-TETRAHYDROPYRANYL)AMINES

| Starting amine | Yield, % | Mp, °C | Formula | Calcd, % C | H | O | Found, % C | H | O |
|---|---|---|---|---|---|---|---|---|---|
| Diphenylamine | 60 | 89–90[a] | $C_{17}H_{17}NO$ | 80.6 | 7.6 | 6.3 | 80.3 | 7.6 | 6.4 |
| Phenoxazine | 85 | 140–141[b] | $C_{17}H_{17}NO_2$ | 76.4 | 6.4 | 12.0 | 76.3 | 6.2 | 12.0 |
| Phenyl-α-naphthylamine | 42 | 115–116[c] | $C_{21}H_{21}NO$ | 83.1 | 7.0 | 5.3 | 83.1 | 7.2 | 5.3 |
| Phenothiazine | 72 | 156–157[b] | $C_{17}H_{17}NOS$ | 72.1 | 6.1 | *d* | 72.1 | 5.8 | *d* |
| 4-Methyl-4′-nitrodiphenylamine | 85 | 99–100[e] | $C_{18}lH_{20}N_2O_3$ | 69.2 | 6.5 | *f* | 69.2 | 6.5 | *f* |

[a] Recrystallized from methanol. [b] Recrystallized from acetonitrile. [c] Recrystallized from petroleum ether (bp 30–60°). [d] *Anal.* Calcd: S, 11.3. Found: S, 11.4. [e] Recrystallized from cyclohexane. [f] *Anal.* Calcd: N, 9.0, Found: N, 8.9.

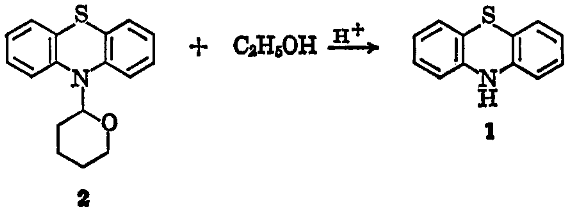
The course of the reaction is illustrated by phenothiazine (1), which reacts with dihydropyran to give 10-(2-tetrahydropyranyl)phenothiazine (2) in 72% yield. The proposed structure of this derivative is in agreement with spectral data. The infrared spectrum showed no N-H stretching band in the 3400-cm.$^{-1}$ region (present in phenothiazine at 3390 cm.$^{-1}$) but contained two strong bands attributed to C–O stretching[7] at 1025 and 1070 cm$^{-1}$. The ultraviolet spectrum (acetonitrile) of the product, $\lambda_{max}$ 251 mμ (ε 31,000) and 298 mμ (ε 3240), was similar to that of phenothiazine, $\lambda_{max}$ 253 mμ (ε 31,900) and 312 mμ (ε 5640). In the nmr spectrum, complex multiplets occurred at 7.1, 4.9, 4.0, and 1.7 ppm. The signal at 7.1 ppm is attributed to the eight aromatic protons, that at 4.9 ppm to the methine proton, the signal at 4.0 ppm to the methylene protons adjacent to oxygen, and that at 1.7 ppm to the remaining six methylene protons. The integrated strengths of these peaks were in the expected ratio of 8:1:2:6.



1

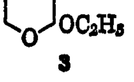
2

All derivatives could be easily decomposed in alcohol to regenerate the starting amine in high yield. No attempt was made to identify the other expected product of this reaction, 2-ethoxytetrahydropyran (3).



2

1



3

Data on derivatives of five secondary aromatic amines are summarized in Table I. The yields are based on single reactions and may be capable of significant improvement.

The sole failure encountered to date has been with 2,4-dinitrodiphenylamine, and is probably due to the combined resonance effects of the two nitro groups and steric hindrance by the *ortho* nitro group.

### Experimental Section

**Methods.**—Analyses were performed by the Analytical Research Branch of the Chemical Research and Development Laboratories. Infrared spectra were recorded using a Perkin-Elmer 521 or a Beckman IR-5A infrared spectrophotometer. All compounds were run as 5% solutions in chloroform. Nmr spectra were recorded using a Varian Associates A-60 nmr spectrometer, and all chemical shifts are given in parts per million downfield from tetramethylsilane. Deuteriochloroform was used as the solvent in all cases. A Beckman DK-2 recording spectrophotometer was used to record ultraviolet spectra. For thin layer chromatography, silica gel G, Merck, was used. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. 3,4-Dihydropyran was distilled and stored over anhydrous potassium carbonate prior to use. All experimental procedures were similar to that described for phenothiazine, with the exception of phenyl-α-naphthylamine. Tetrahydrofuran was used as the solvent with this amine, since no reaction occurred in diethyl ether.

**10-(2-Tetrahydropyranyl)phenothiazine** (2).—To a slurry of 15.0 g (0.0755 mole) of phenothiazine in 20 ml of anhydrous ether was added 13.8 g (0.164 mole) of dihydropyran and 1 drop of concentrated sulfuric acid (sp gr 1.84). The phenothiazine dissolved completely within 30 sec and a mildly exothermic reaction continued for 2 min. After 4 min, the adduct began to precipitate. It was then filtered and washed with 250 ml of 5% sodium carbonate solution. The adduct was dissolved in boiling acetonitrile and recrystallized as the solution cooled to room temperature. A total of 15.1 g (72% yield) was obtained. After two additional recrystallizations from acetonitrile, an analytical sample had mp 156–157°.

*Anal.* Calcd for $C_{17}H_{17}NOS$: C, 72.05; H, 6.05; S, 11.31. Found: C, 72.1; H, 5.8; S, 11.4.

**Regeneration of Phenothiazine.**—A total of 15.1 g (0.0533 mole) of 10-(2-tetrahydropyranyl)phenothiazine was partially dissolved in 50 ml of boiling ethanol. When 1 drop of concentrated sulfuric acid (sp gr 1.84) was added, the solution turned dark brown and the compound dissolved completely. As the solution cooled, yellow crystals of phenothiazine precipitated. A total of 10.6 g (quantitative yield) was obtained. After drying, the crystals had mp 183–184.5°, lit.[8] mp 183–185°. A mixture melting point with an authentic sample of phenothiazine showed no depression.

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(7) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 119.

(8) B. E. Baker and L. Brickman, *J. Am. Chem. Soc.*, **67**, 1223 (1945).

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## Substituent Effects in Photochromic Nitrobenzylpyridines

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Previous investigations showed that many derivatives of 2-(2-nitrobenzyl)pyridine[1-3] and related compounds[4]

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(1) J. A. Sousa and J. Weinstein, *J. Org. Chem.*, **27**, 3155 (1962).

(2) A. L. Bluhm, J. Weinstein, and J. A. Sousa, *ibid.*, **28**, 1989 (1963).

(3) J. Weinstein, J. A. Sousa, and A. L. Bluhm, *ibid.*, **29**, 1586 (1964).

(4) A. L. Bluhm, J. A. Sousa, and J. Weinstein, *ibid.*, **29**, 636 (1964); J. D. Margerum *et al.*, *J. Phys. Chem.*, **66**, 2434 (1962).

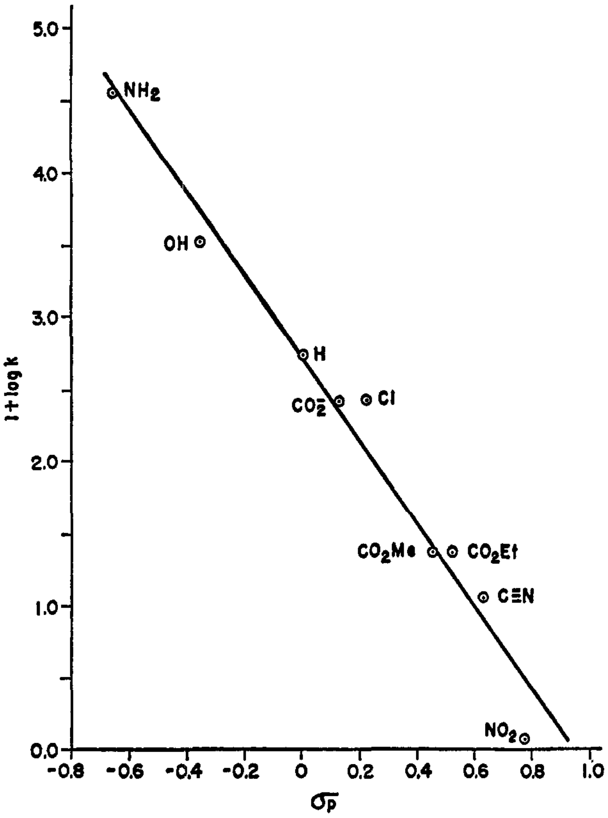
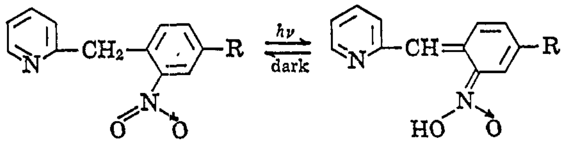


Figure 1.—Plot of log $k$ values *vs.* Hammett $\sigma_p$ constants.

are photochromic in solution in ethanol and other solvents. Common to all of these aromatic compounds is the structural feature of a nitro and -C-H group *ortho* to each other.[1-5] It is believed that the color change produced by ultraviolet irradiation is due to the formation of the tautomeric *aci*-nitro structure.[1,6-8]



Rate measurements of the fading reaction in organic solvents of several derivatives of 2-(2-nitrobenzyl)pyridine were carried out.[1-3] The reaction was found to proceed by first-order kinetics with an activation energy in ethanol of about 5 kcal/mole and an entropy of activation of *ca.* −45 eu. Also, it was found that the rate of the reaction is affected by the nature of the substituent in the *para* position of the benzene ring. This observation prompted us to extend the group of compounds previously reported and study the effect of *para* substituents on the rate of the dark reaction.

Rate measurements were carried out in ethanol at room temperature by flash photolysis techniques. In every case studied, the fading process was found to follow first-order kinetics. The values of the rate constant, $k$, for the fading reaction are listed in Table I and can be seen to be markedly sensitive to the electronegativity of the *para* substituent. For example, in going from $NO_2$ to $NH_2$ the value of $k$ is enhanced by a factor of $10^4$. Also, the rate constant is almost 500 times greater when H rather than $NO_2$ is the *para* substituent.

TABLE I

VALUES OF $k$ AND $t_{1/2}$ FOR THE FADING REACTIONS OF 2-(2-NITRO-4-SUBSTITUTED BENZYL)PYRIDINES IN ETHANOL AT 25°

| 4-Substituent | $k$ sec$^{-1}$ | $t_{1/2}$, msec | $\sigma_p$[a] |
|---|---|---|---|
| $NH_2$ | $370 \times 10^1$ | 0.187 | −0.660 |
| OH | 329 | 2.11 | −0.357 |
| H | 56.3 | 12.3 | 0 |
| Cl | 27.4 | 25.3 | 0.227 |
| $CO_2^-$ | 26.3 | 26.3 | 0.132 |
| $CONH_2$ | 5.94 | 117 | |
| $CO_2Et$ | 2.45 | 283 | 0.522 |
| $CO_2Me$ | 2.42 | 286 | 0.463 |
| C≡N | 1.17 | 592 | 0.628 |
| $NO_2$ | 0.122 | $568 \times 10^1$ | 0.778 |

[a] Values given by H. H. Jaffé, *Chem. Rev.*, **53**, 222 (1953), except the value for the $CO_2Me$ group, which was determined by H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. Trav. Chim.*, **78**, 815 (1959).

The greater the electron-repelling power of the substituent, the faster the reaction proceeds. In Figure 1, log $k$ values are shown to be linearly proportional to Hammett $\sigma$ values.[9] The value of the reaction constant ($\rho$) for the least-square line is −2.85, and the correlation coefficient for the line is 0.986. The correlation is considered excellent on the arbitrary scale proposed by Jaffe.[10] A $\sigma_p$ value was not found in the literature for the $CO-NH_2$ group. This work suggests a value of 0.33.

The observed substituent effect is probably due to differences in energy of activation, since it was found previously for the dark reactions of the $p$-C≡N and $p$-$NO_2$ derivatives that the energy of activation differs while the value of the entropy of activation is the same.[1]

### Experimental Section

**2-(2-Nitro-4-chlorobenzyl)pyridine.**—A magnetically stirred solution of 3.0 g (0.013 mole) of 2-(2-nitro-4-aminobenzyl)pyridine[1] and 3.4 ml (0.039 mole) of concentrated hydrochloric acid in 5.0 ml. of water was cooled to 0°, and the amine diazotized by the gradual addition of 0.90 g (0.013 mole) of sodium nitrite in 5.0 ml of water. The diazonium solution was then added to a magnetically stirred, cooled solution of freshly prepared cuprous chloride in 5.7 ml of concentrated hydrochloric acid. The reaction mixture was allowed to warm gradually to room temperature, heated on a steam bath for 1 hr, cooled, and made basic with 5% sodium hydroxide. Solids were collected on a filter. They and the filtrate were extracted several times with benzene. The combined extracts were washed with 3% sodium hydroxide and water, and then dried over anhydrous magnesium sulfate. Evaporation of the benzene gave 1.5 g of a brown viscous liquid. After two distillations at reduced pressure, there was obtained 0.95 g of a light yellow oil.

*Anal.* Calcd for $C_{12}H_9ClN_2O_2$: C, 57.96; H, 3.65; Cl, 14.26; N, 11.27. Found: C, 58.12; H, 3.80; Cl, 13.99; N, 11.28.

**2-(2-Nitro-4-hydroxybenzyl)pyridine.**—A magnetically stirred solution of 3.0 g (0.013 mole) of 2-(2-nitro-4-aminobenzyl)pyridine[1] and 2.94 ml (0.052 mole) of concentrated sulfuric acid in 4.0 ml of water was cooled to 0°. Diazotization was carried out at 0–5° by the gradual addition of 0.90 g (0.013 mole) of sodium nitrite in 4.0 ml of water. The resulting red paste was added to a continuously boiling solution of 4.0 ml of concentrated sulfuric acid in 20 ml of water. The solution was then cooled to room temperature; precipitated solids were removed by filtration. To the filtrate 3% sodium hydroxide was added gradually. A sizeable crop of unidentified material separated and was removed by filtration from the still slightly alkaline reaction mixture. On

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(5) G. Wettermark, *Nature*, **194**, 677 (1962).

(6) R. Hardwick and H. S. Mosher, *J. Chem. Phys.*, **36**, 1402 (1962).

(7) A. Ficalbi, *Gazz. Chim. Ital.*, **93**, 1530 (1963).

(8) H. Morrison, and B. H. Migdalof, *J. Org. Chem.*, **30**, 3996 (1965).

(9) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p 184.

(10) See Table I, ref *a*, p 236.

continued careful neutralization a small amount of material precipitated and was collected on a filter. Several recrystallizations from ethanol gave 62 mg of pale yellow crystals, mp 139–140°. The infrared spectrum showed the presence of an OH group in the molecule.

*Anal.* Calcd for $C_{12}H_{10}N_2O_3$: C, 62.60; H, 4.38. Found: C, 61.91; H, 4.60.

**Sodium Salt of 2-(2-Nitro-4-carboxybenzyl)pyridine.**—To 2-(2-nitro-4-carboxybenzyl)pyridine[2] (0.1987 g) in 5 ml of water a stoichiometric amount of standardized sodium hydroxide solution was added. The solution was then clarified by filtration, and the filtrate was evaporated to dryness with a current of nitrogen. The white residue was recrystallized three times from a mixture of ethanol and acetone. An infrared spectrum showed strong absorptions at 1410 and 1615 $cm^{-1}$ characteristic for the carboxylate anion group. (The precursor acid showed the carboxylic acid group at 1712 $cm^{-1}$.) The preparation of all the other compounds was described previously.[1,2,11]

*Anal.* Calcd for $C_{13}H_9N_2NaO_4$: C, 55.71; H, 3.24; N, 10.00. Found: C, 55.63; H, 3.13; N, 9.74.

**Kinetic Measurements.**—Samples for rate measurements were recrystallized or redistilled at reduced pressure before use. 2-(2-Nitro-4-aminobenzyl)pyridine was purified by chromatographic adsorption on a silica gel (Davison Chemical Co., grade 950) column and elution with 95% benzene–5% ethyl acetate, followed by recrystallization from ethanol to give bright yellow crystals, mp 127–128°. Spectro Grade absolute alcohol was used to prepare $10^{-4}$ *M* solutions.

The flash photolysis equipment and techniques used for the kinetic studies were described previously.[1,12] Measurements were made at 25°. The decrease in absorbance of the visible absorption band produced by ultraviolet irradiation was followed at 580 mμ with respect to time for all compounds except 2-(2-nitrobenzyl)pyridine and 2-(2-nitro-4-aminobenzyl)pyridine. For these compounds the dark reaction was followed at 400 and 500 mμ, respectively.

Values of the first-order rate constant, *k*, were calculated from the slope of the straight line in plots of log optical density *vs.* time. The reactions were followed for at least three half-lives.

**Acknowledgment**—We wish to thank Mr. F. Bissett for the preparation of 2-(2-nitrobenzyl)pyridine and Mr. C. DiPietro for the chemical analyses.

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(11) A. J. Nunn and K. Schofield, *J. Chem. Soc.*, 583 (1952).

(12) L. Lindqvist, *Rev. Sci. Instr.*, **35**, 993 (1964).

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# Aralkyl Hydrodisulfides. VI. The Reaction of Benzhydryl Hydrosulfide with Several Nucleophiles

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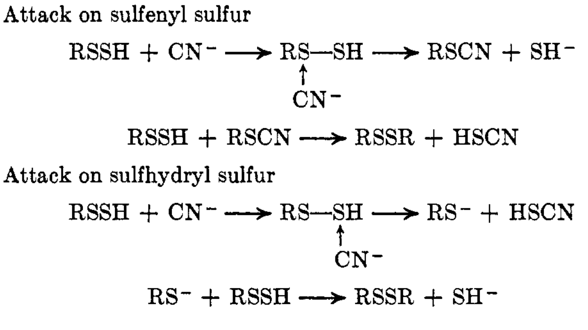
In a previous paper,[1] reactions of benzyl hydrodisulfide with several inorganic anions and benzenethiolate ion were studied. It was reported that hydroxide and sulfite ions, which have weak nucleophilicity toward sulfur, attack initially the sulfenyl sulfur atom of the hydrodisulfide, yielding about 0.5 mole each of hydrogen sulfide and diaralkyl disulfide and various amounts of the other products but no thiol, and also that cyanide and thiolate ions having strong nucleophicity attack both sulfenyl and sulfhydryl sulfur. Attack on sulfhydryl sulfur was postulated to give the thiol besides other sulfur-containing compounds. In the reaction mechanism, any steric factor of the substrate of the reactants was not taken into consideration. In the present paper several inorganic anions and benzenethiolate ion were allowed to react with benzhydryl (diphenylmethyl) hydrodisulfide which may suffer steric hindrance as compared with the benzyl compound. The reactions were carried out under conditions similar to previous ones[1] and indicated similar features. The products are summarized in Table I. The variety and amounts of the products from the reaction of benzhydryl hydrodisulfide with hydroxide ion are quite similar to those from the benzyl compound. Therefore, the reaction seems to proceed through the same mechanism as reported in previous paper, *i.e.*, through sulfenyl sulfur attack. In the reactions of benzhydryl hydrodisulfide with cyanide and benzenethiolate ions, the distribution of the products was not greatly different from that from the benzyl hydrodisulfide reaction in the previous paper. However, a slight dissimilarity was observed about a little increased amount of the thiol in Table I compared with the corresponding one in the previous paper. This suggests that the attack on sulfenyl sulfur atom was sterically hindered, and that the attack on the alternative sulfhydryl sulfur contributed to the reaction more predominantly than in the case of the benzyl compound.

The most prominent distinction between the results in Table I and those in the previous paper is that in the reaction of benzhydryl hyrodisulfide with sulfite ion about 0.1 mole of diphenylmethanethiol was obtained from 1 mole of the hydrodisulfide, while the thiol was reported not to be detected from benzyl hydrodisulfide.[1] The formation of a detectable amount of the thiol may be interpreted by assuming that sulfhydryl sulfur attack contributes to the reaction at the expense of the sulfenyl sulfur attack by analogy with the above discussion. However, this presumption is denied for the following reason. The distribution of the products with cyanide will be discussed as representative of the mechanism for both sulfenyl and sulfhydryl sulfur attacks. In the case of benzenethiolate the distribution is made complexing because of the participation of benzenethiolate in the products and therefore kept away. The reaction mechanism with cyanide is again cited (Scheme I) from the previous paper.[1]

Scheme I



Attack on sulfenyl sulfur

$$\mathrm{RSSH + CN^- \longrightarrow \underset{\overset{\uparrow}{CN^-}}{RS{-}SH} \longrightarrow RSCN + SH^-}$$

$$\mathrm{RSSH + RSCN \longrightarrow RSSR + HSCN}$$

Attack on sulfhydryl sulfur

$$\mathrm{RSSH + CN^- \longrightarrow \underset{\overset{\uparrow}{CN^-}}{RS{-}SH} \longrightarrow RS^- + HSCN}$$

$$\mathrm{RS^- + RSSH \longrightarrow RSSR + SH^-}$$

A detailed examination of Scheme I leads to the relationships that the amount of the diaralkyl disulfide is equal to that of hydrogen sulfide, and that the amount of thiocyanate is equal to the sum of the amounts of thiol and hydrogen sulfide (or the disulfide), whatever

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[1] Part IV: S. Kawamura, Y. Otsuji, T. Nakabayashi, T. Kitao, and J. Tsurugi, *J. Org. Chem.*, **30**, 2711 (1965).