

## Experimental Section

*p*-Nitroperoxybenzoic acid was prepared and purified according to the procedure of Silbert, *et al.*<sup>8</sup> All the solvents used were Reagent grade commercial products and were dried and distilled before use. The purity of each was confirmed by vapor phase chromatography. *trans*-Stilbene, scintillation grade, was obtained from Fluka and used without further purification.

The infrared spectra were recorded at 20° on a Perkin-Elmer Model 521 infrared spectrophotometer using 0.05–0.10 mm cells (NaCl). Methylene chloride solutions of equimolar amounts of peroxy acid and a compound with basic oxygen were employed.

The kinetics of epoxidation was followed iodometrically according to Lynch and Pausacker.<sup>9</sup> Reactions were performed in 50-ml volumetric flasks. Samples (5 ml) were quenched in 2-N sulfuric acid cooled and degassed with small pinches of Dry Ice, an excess of potassium iodide was added (1 ml of 15% solution), and the liberated iodine was titrated with 0.05 N sodium thiosulfate without starch indicator. When ethyl acetate or diethyl ether were used as solvents, carbon tetrachloride was necessary to add to the titration mixture in order to obtain satisfactory end-points. Observed titres were corrected for the decomposition of peroxy acid in the corresponding solvent. Second-order rate constants were obtained from a linear least-squares program. Calculation of activation energies and entropies was performed by the usual method.<sup>10</sup> Errors (standard deviations) in second-order rate constants are  $\pm 2\%$ , those in  $E_a$  are *ca.*  $\pm 0.5$  kcal/mol, and those in  $\Delta S^\ddagger$  are  $\pm 1.5$  eu.

**Registry No.**—*trans*-Stilbene, 103-30-0; *p*-nitroperoxybenzoic acid, 943-39-5.

**Acknowledgment.**—The authors wish to thank Professor D. Hadži for his interest and encouragement. The financial support of this research by the Boris Kidrič Fund is also gratefully acknowledged.

(8) L. S. Silbert, E. Siegel, and D. Swern, *J. Org. Chem.*, **27**, 1136 (1962).

(9) B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955).

(10) J. F. Bunnett, "Investigation of Rates and Mechanisms of Reaction," Part I, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1961.

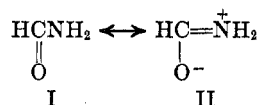
### $pK_a$ Values of 4-Substituted 4'-Aminobenzanilides and 4'-Hydroxybenzanilides. A Search for Transmission of Electronic Effects through an Amide Linkage

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The planarity and restricted rotation of amide groups have been attributed to a dipolar resonance contributor II. Pauling<sup>1</sup> has estimated that I and

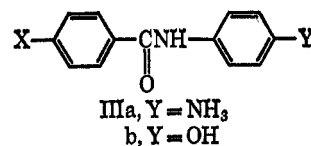


II contribute 60 and 40%, respectively, corresponding to 40% double-bond character for the C–N bond. One might expect, therefore, that two aromatic rings joined by an amide group would be conjugatively linked *via* the partial double bond. We show below that,

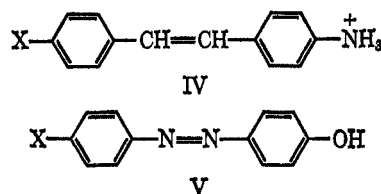
(1) L. Pauling, "Symposium on Protein Structure," A. Newberger, Ed., John Wiley & Sons, Inc., New York, N. Y., 1958, p 17.

on the contrary, there is no conjugative transmission in the ground states of compounds III.<sup>2</sup>

The degree of electronic interaction between the aromatic rings of IIIa and IIIb was estimated from



the  $pK_a$  values presented in Table I. Since the  $pK_a$  values of the corresponding stilbenes (IV) and azoben-



zenes (V) are known,<sup>3–5</sup> it is possible to compare the amide group with the ethylene and azo functionalities.

TABLE I  
 $pK_a$  VALUES OF 4-SUBSTITUTED 4'-AMINOBENZANILIDES AND 4'-HYDROXYBENZANILIDES (IIIa AND IIIb)<sup>a</sup>

Y	X	$pK_a$
$\text{NH}_3^+$	$\text{OCH}_3$	4.62
$\text{NH}_3^+$	$\text{CH}_3$	4.52
$\text{NH}_3^+$	H	4.55
$\text{NH}_3^+$	Cl	4.54
$\text{NH}_3^+$	$\text{NO}_2$	4.48
OH	$\text{OCH}_3$	9.55
OH	$\text{CH}_3$	9.54
OH	H	9.54
OH	Cl	9.50
OH	$\text{NO}_2$	9.50

<sup>a</sup> Determined spectrophotometrically in 1.6% acetonitrile-water at 25.0°.

The Hammett  $\rho$  value for IIIa, calculated from the data in Table I, was found to be  $0.09 \pm 0.04$  in 1.6% acetonitrile-water. This is considerably less than the  $\rho$  value for ionization of IV (0.422<sup>3</sup> and 0.684<sup>4</sup> in ethanol-water). The small  $\rho$  for IIIa cannot be attributed to an unusually small double-bond character of the amide C–N bond because the benzanilides show normal amide carbonyl bands in the infrared and because the presence of two phenyl rings should, if anything, enhance the contribution from the dipolar structure II. However, the possibility existed that resonance between the phenyl rings was unimportant in the conjugate base of IIIa because this would lead to a tetrapolar contributor. For this reason we determined the  $pK_a$  values of IIIb, a system

(2) Conjugation in the excited state of benzanilides has been demonstrated by V. A. Izmail'skii and A. V. Malygina, *Zh. Obshch. Khim.*, **29**, 3935 (1959).

(3) H. Veschambre and A. Kergomard, *Bull. Soc. Chim. Fr.*, 336 (1966).

(4) M. Syz and H. Zollinger, *Helv. Chim. Acta*, **48**, 517 (1965).

(5) S. Yeh and H. H. Jaffé, *J. Amer. Chem. Soc.*, **91**, 3287 (1969).

TABLE II  
MELTING POINTS AND ANALYSES OF 4-SUBSTITUTED 4'-HYDROXYBENZANILIDES

XC <sub>6</sub> H <sub>4</sub> - CONHC <sub>6</sub> H <sub>4</sub> OH, X	Mp, °C	Calcd, %			Found, %		
		C	H	N	C	H	N
OCH <sub>3</sub>	230-232	69.12	5.39	5.76	68.96	5.44	5.71
CH <sub>3</sub>	215-216	73.99	5.77	6.16	74.00	5.73	6.10
Cl	245-246	63.04	4.07	5.65	62.99	3.96	5.50
NO <sub>2</sub>	265-266	60.46	3.90	10.85	60.44	3.77	10.77

in which resonance stabilization of the conjugate base (phenolate anion) results in dispersal of charge rather than in charge creation. The  $\rho$  value for ionization of IIIb in 1.6% acetonitrile-water was found to be  $0.05 \pm 0.02$ . This is 10 times less than the  $\rho$  for ionization of V (20% ethanol-water) and 6 times less than the  $\rho$  for ionization of substituted 4-hydroxystilbenes (1.6% acetonitrile-water).<sup>6</sup> Clearly, the amide linkage is a poor transmitter of electronic effects despite the considerable double-bond character of the C-N bond.<sup>7</sup>

In recent work, Johnson and coworkers<sup>9</sup> showed that Michael addition of ethanol to acrylanilides and elimination of HBr from  $\beta$ -bromopropionanilides (ethanol, 55°) have a Hammett  $\rho$  of 1.77 and 1.74, respectively. The amide linkage, it was concluded, is an excellent transmitter of activation effects. On the basis of our results with the benzanilide systems, it would appear that the large  $\rho$  values for the addition and elimination reactions are due mainly to an efficient transmission of polar effects, and that there is little direct resonance interaction between the substituents and the reactive sites.

The reason for the lack of electronic transmission through the amide linkage is not clear. Perhaps the 60% reduction in double-bond character is sufficient to suppress completely any conjugative effects. Alternatively, the nature of the partial double bond of the amide group may be different from that of ethylenic and azo double bonds. The partial double bond of the amide could involve overlap between the unshared pair of electrons on the nitrogen and an empty carbon orbital in the 3 shell. This is consistent with an amide carbonyl bond length that is shorter than that of acetaldehyde.<sup>10</sup> Our results might also be related to Pauling's idea that polarization of the  $\sigma$  bond between the carbonyl carbon and the nitrogen effectively liberates a  $p$  orbital of carbon lying in the plane of the group, and permits a  $\pi$  bond to be formed with an unshared pair of electrons on the oxygen.<sup>1</sup>

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**Compounds.**—The general procedure used for the preparation of the substituted 4'-hydroxybenzanilides was as follows. A *para*-substituted benzoyl chloride (0.01 mol) was dissolved in 20

(6) The  $\rho$  was determined from a two-point Hammett plot.

(7) The ionization of *para*-substituted *N*-methylbenzhydroxamic acids has a  $\rho$  of 0.86 in 80% Methyl Cellulosolve-water.<sup>8</sup> This  $\rho$  is less than that for the ionization of benzoic acid in water, and it suggests that there may be also little direct resonance interaction through the carbonyl carbon-nitrogen bond of the hydroxamic acids. Moreover, the  $pK_a$  values correlate with  $\sigma$  rather than with  $\sigma^-$ .

(8) O. Exner and W. Simon, *Collect. Czech. Chem. Commun.*, **30**, 4078 (1965).

(9) H. W. Johnson, E. Ngo, R. C. Stafford, and Y. Iwata, the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Organic Abstract No. 31.

(10) H. A. Bent, *Chem. Rev.*, **68**, 587 (1969).

ml of pyridine that had been dried over Linde 4A Molecular Sieve. This solution was added dropwise to 20 ml of a pyridine solution of recrystallized *p*-hydroxyaniline (0.01 mol). The reaction mixture was then boiled under reflux for 12 hr, after which the pyridine was removed with the aid of a rotary evaporator. The residue was crystallized from ethanol-water and sublimed. The properties of the products are given in Table II.

Substituted 4'-aminobenzanilides were prepared by the method of Izmail'skii and Malygina.<sup>2</sup>

**$pK_a$  Determinations.**—The  $pK_a$  values of the benzanilides and stilbenes were determined spectrophotometrically by the method of Albert and Serjeant.<sup>11</sup>

**Registry No.**—IIIa (X = OCH<sub>3</sub>), 23600-43-3; IIIa (X = CH<sub>3</sub>), 23600-44-4; IIIa (X = H), 17625-83-1; IIIa (X = Cl), 23600-46-6; IIIa (X = NO<sub>2</sub>), 6409-40-1; IIIb (X = OCH<sub>3</sub>), 23600-48-8; IIIb (X = CH<sub>3</sub>), 23646-69-7; IIIb (X = H), 15457-50-8; IIIb (X = Cl), 19207-92-2; IIIb (X = NO<sub>2</sub>), 13160-56-0.

**Acknowledgment.**—This work was supported in part by a grant from the National Science Foundation.

(11) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," Methuen and Co. Ltd., London, 1962, p 69.

### Stereochemistry of $\alpha$ -Phenethyl Radical Dimerization<sup>1</sup>

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It has been reported<sup>3</sup> that the reduction of  $\alpha$ -bromoethylbenzene and  $\alpha$ -chloroethylbenzene by chromous sulfate produces 85–90% *meso*-2,3-diphenylbutane and 10–15% the *dl* forms, the disparity being attributed to conformational effects. If correct, this observation would connote a mechanism of final product formation other than simple dimerization of free radicals, because there is abundant qualitative and semiquantitative evidence<sup>4</sup> based on yields in other free-radical situations

(1) Work was supported by the Atomic Energy Commission.

(2) Summer Student Training Program, Argonne National Laboratory, 1969, supported in part by the National Science Foundation.

(3) C. E. Castro and W. C. Kray, Jr., *J. Amer. Chem. Soc.*, **85**, 2768 (1963).

(4) Comparable yields of *meso*- and *dl*-2,3-diphenylbutane have been reported in (a) the reaction of  $\alpha$ -chloroethylbenzene with magnesium and moist ether [E. Ott, *Chem. Ber.*, **61**, 2124 (1928)]; (b)  $\alpha$ -bromoethylbenzene with sodium [K. T. Serijan and P. H. Wise, *J. Amer. Chem. Soc.*, **74**, 365 (1952)]; (c)  $\alpha$ -bromoethylbenzene with magnesium and cupric chloride [J. B. Conant and A. H. Blatt, *ibid.*, **50**, 551 (1928)]; (d) coupling of Grignard reagent [W. T. Somerville and P. E. Spoerri, *ibid.*, **74**, 3803 (1952)]; (e) decomposition of diacetyl peroxide in ethylbenzene [M. S. Kharasch, H. McBay, and W. H. Urry, *J. Org. Chem.*, **10**, 401 (1945)]; (f) decomposition of di-*t*-butyl peroxide in ethylbenzene [E. H. Farmer and C. G. Moore, *J. Chem. Soc.*, **1951**, 131]; (g) decomposition of benzoyl peroxide in ethylbenzene [R. L. Dannley and B. Zaremsky, *J. Amer. Chem. Soc.*, **77**, 1588 (1955)]. In one instance, the reaction of hydrotropoyl chloride with sodium peroxide, the equality of yields was established by careful ir analysis [F. D. Greene, *ibid.*, **77**, 4869 (1955)].