101°; nmr ($CDCl_3$) δ 2.35 [s, $N(CH_3)_2$], 2.98 (s, NCH_3), and 6.4–7.2 (m, $2C_6H_5$).

Anal. Calcd for $C_{16}H_{19}N_3$: C, 75.9; H, 7.6; N, 16.6. Found: C, 76.1; H, 7.7; N, 16.4.

The ethanol–ether filtrate remaining after isolation of the hydriodide was diluted with a large volume of ether to give 5.0 g of solid material, mp 179–190°. Three recrystallizations from water gave 0.40 g of N^1,N^1,N^2,N^3-tetramethyl-N^3-phenylbenzamidrazonium iodide (**9**),[12] mp 243–244°. The infrared spectrum of this product was identical with that of the amidrazonium salt prepared by the following procedure.

A solution containing 2.0 g of 1,1,2-trimethyl-2-(*N*-phenylbenzimodoyl)hydrazine (**7**) in 5 ml of methyl iodide was allowed to stand for 24 hr. Dilution with ether gave 1.1 g of crude product, mp 230–235°. An additional 2 ml of methyl iodide was added to the evaporated filtrate and a second crop, 1.6 g, mp 238–242°, was collected after 5 days. Recrystallization from ethanol gave white crystals: mp 245–246°: nmr (D_2O, 85°) δ 2.91 [s, $N(CH_3)_2$], 3.41 (s, NCH_3), 3.91 (s, NCH_3), 7.92 (s, C_6H_5), and 8.10 (s, C_6H_5).

Anal Calcd for $C_{17}H_{22}IN_3$: C, 51.7; H, 5.6; N, 10.6; I, 32.1. Found: C, 51.3; H, 5.8; N, 10.6; I, 32.1.

1,1,2-Trimethyl-2-(*N*-phenylbenzimidoyl)hydrazine (7).—*N*-Phenylbenzimidoyl chloride (14.0 g) was added to a solution of 10.0 g of 1,1,2-trimethylhydrazine[14] in 30 ml of dry benzene. After 6 days at room temperature, the reaction mixture was evaporated to give a solid residue from which the product (10.5 g, mp 99–100°) was extracted with boiling petroleum ether. The nmr spectrum of the product was identical with that of the product obtained by the methylation of **2**.

Preparation of *N*-Methylbenzanilide Dimethylhydrazone Hydriodide (8 HI).—Condensation of *N*-methylbenzanilide with 1,1-dimethylhydrazine was carried out by the procedure of Rapoport and Bonner[13] on a 0.1-mol scale utilizing a 12-hr reflux period. The oily product was dissolved in 40 ml of ethanol and treated with 15 ml of 57% hydriodic acid. Dilution with ether gave 7.2 g (19%) of the **hydriodide**, mp 233–236°. Recrystallization from ethanol gave white crystals: mp 245–246°; nmr (D_2O, 85°) δ 3.18 [s, $N(CH_3)_2$], 3.95 (s, NCH_3), 7.8–8.1 (m, $2C_6H_5$).

Anal. Calcd for $C_{16}H_{20}IN_3$: C, 50.4; H, 5.3; N, 11.0; I, 33.3. Found: C, 50.6; H, 5.3; N, 11.1; I, 33.3.

The **free base 8** was obtained by extraction of a solution containing 7.2 g of the hydriodide in 250 ml of 6 *N* NaOH with three 100-ml portions of chloroform. Evaporation of the dried solution gave 4.0 g of the oily amidrazone: nmr ($CDCl_3$) δ 2.70 [s, $N(CH_3)_2$], 3.22 (s, NCH_3), and 6.6–7.8 (m, $2C_6H_5$).

N^1,N^1,N^1,N^3-Tetramethyl-N^3-phenylbenzamidrazonium Salts (10).—The **iodide** was prepared by treating the free base (from 2.4 g of the hydriodide) with 3 ml of methyl iodide. After 24 hr, dilution with ether gave the crude product as an oil which after trituration with ether gave 1.7 g of white solid, mp 162–165°. Recrystallization from ethanol gave white crystals: mp 166–167°; nmr (DMSO-d_6) δ 3.31 [s, $N^+(CH_3)_3$ and NCH_3] and 7.2–7.7 (m, $2C_6H_5$).

Anal. Calcd for $C_{17}H_{22}IN_3$: C, 51.7; H, 5.6; N, 10.6; I, 32.1. Found: C, 51.9; H, 5.3; N, 10.6; I, 32.5.

Reaction of the amidrazone with CD_3I gave the deuterated salt **11**, mp 157–160°. The nmr spectrum (DMSO-d_6) showed the correct (10:9) aromatic:methyl integration.

The **fluoroborate** was obtained by treatment of a saturated aqueous solution of the iodide with 1 equiv of sodium fluoroborate and recrystallized from ethanol–ether as white crystals, mp 138–139°. The nmr spectrum was identical with that of the iodide.

Anal. Calcd for $C_{17}H_{22}BF_4N_3$: C, 57.2; H, 6.2; N, 11.8. Found: C, 57.2; H, 6.2; N, 11.7.

The **tosylate** was obtained by heating 2.0 g of the amidrazone and 2 ml of methyl tosylate on the steam bath for 2 hr. The oily salt was precipitated with ether, washed with ether several times, and dried *in vacuo* at 100°: nmr (DMSO-d_6) δ 3.22 [s, $(CH_3)_3N^+$ and CH_3N], 2.22 (s, $CH_3C_6H_4SO_3^-$), and 7.1–8.0 (m, aromatic). The nmr spectrum showed the salt to be contaminated with methyl tosylate: δ 2.31 (s, CCH_3) and 3.68 (s, OCH_3).

Hydrolysis of N^1,N^1,N^1,N^3-Tetramethyl-N^3-phenylbenzamidrazonium Salts (10).—A solution of the iodide (0.9 g) in 25 ml of 6 *N* HCl was heated under reflux for 2 days. Iodide sublimed in the condenser. On cooling, 0.10 g of benzoic acid (mp and mmp 118–120°) crystallized and was filtered off. The filtrate was made basic with sodium carbonate and extracted with chloroform. Evaporation of the dried solution gave an oil which was suspended in 10 ml of 6 *N* NaOH and shaken with 0.5 ml of benzenesulfonyl chloride giving crude *N*-methyl-*N*-phenylbenzenesulfonamide, 0.15 g, mp 69–75°. One recrystallization from aqueous ethanol gave mp 72–74° (*lit.*[15] 79°). Identity was established by ir and nmr ($CDCl_3$) δ 3.08 (s, NCH_3) and 6.9–7.7 (m, $2C_6H_5$).

When the deuterated iodide **11** was hydrolyzed as described above, the nmr spectrum of the *N*-methyl-*N*-phenylbenzenesulfonamide showed integrated methyl:aromatic intensity ratios (3:10) that indicated complete absence of NCD_3.

The **tosylate salt** (1.0 g) was hydrolyzed as described above. After filtration of the benzoic acid, the filtrate was divided in half. One-half was treated as before to give the benzenesulfonyl derivative, mp 69–75°. The other half was evaporated, *in vacuo*, to an oil which was dissolved in ethanol, filtered from insoluble material, and reprecipitated twice from ether. The crude product partially solidified on standing. Its nmr spectrum (D_2O) exhibited all of the characteristics of authentic 1,1,1-trimethylhydrazinium tosylate plus contamination by ethanol and minor impurities at δ 7.25 (s) and 2.25 (m).

1,1,1-Trimethylhydrazinium Tosylate.—The salt was obtained in quantitative yield by slowly adding methyl tosylate to an ice-cooled solution of 1,1-dimethylhydrazine in ether. The product was recrystallized from ethanol as white crystals: mp 220–222°; nmr (D_2O) δ 1.98 (s, CH_3C), 3.05 [s, $(CH_3)_3N^+$], and 7.05, 7.58 (d, J = 7 Hz, aromatic AB).

Anal. Calcd for $C_{10}H_{18}N_2O_3S$: C, 48.8; H, 7.4; N, 11.4. Found: C, 49.0; H, 7.8; N, 11.5.

Registry No.—**2**, 27808-65-7; **2** picrate, 27808-66-8; **2** HI, 27808-67-9; **6**, 27808-68-0; **7**, 27873-63-8; **7** HI, 27928-68-3; **7** MeI, 27808-69-1; **8**, 27808-70-4; **8** HI, 27808-71-5; **10** iodide, 27808-72-6; **10** fluoroborate, 27808-73-7; **10** tosylate, 27808-74-8; **10** benzenesulfonyl derivative, 27808-75-9; **11**, 27808-76-0; 1,1,1-trimethylhydrazinium tosylate, 27808-77-1.

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(12) Completely substituted amidrazonium salts have apparently not been previously prepared. We have adopted the nomenclature proposed by Rapoport and Bonner (ref 13) and recommended in ref 4 for naming these salts.

(13) H. Rapoport and R. M. Bonner, *J. Amer. Chem. Soc.*, **72**, 2783 (1950).

(14) J. B. Closs, J. H. Aston, and T. S. Oakwood, *ibid.*, **75**, 2937 (1953).

(15) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, Wiley, New York, N. Y., 1964, p 332.

Quinoxaline Studies. XVIII.[1] Unequivocal Syntheses of 2-Amino-6- and -7-chloroquinoxalines

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Discussion

2-Amino-6- (or 7-) chloroquinoxalines have two known biomedical utilities: as a sulfaquinoxaline[2] and

(1) Paper XVII of this series: H. R. Moreno and H. P. Schultz, *J. Med. Chem.*, **13**, 1005 (1970).

(2) F. J. Wolf, R. H. Beutel, and J. R. Stevens, *J. Amer. Chem. Soc.*, **70**, 2572 (1948).

as a substance pertinent to the structure proof of 7- (or 8-) chloroalloxazine, a diuretic.[3] Although some structural evidence has been published, until now the structures of the 6- and 7-chloro derivatives of 2-aminoquinoxaline have not, in fact, been clearly delineated.

The purpose of this paper is to report the unequivocal syntheses of 2-amino-6- and -7-chloroquinoxalines, to compare the physical properties of these newly prepared substances with the properties of those earlier reported,[2,3] and to present evidence that the heretofore described materials were in all instances mixtures of the two isomers.

Recently published descriptions[1] of the syntheses and structure proofs of the 6- and -7-chloro-2-quinoxalinecarboxylic acids provided means for the preparations of the target aminochloroquinoxalines *via* the sequence carboxylic acid, methyl carboxylate, carboxamide, and amine.

Initial work demonstrated that 2-quinoxalinecarboxamide readily underwent the traditional Hofmann hypohalite degradation to the corresponding amine. Unfortunately, the 6- and -7-chloro-2-quinoxalinecarboxamides failed to yield amines under the same circumstances but were recovered unchanged from the reaction mixtures.

A measure of success was finally attained in this critical step by performing the Hofmann degradation of amide to amine in cold, commercial bleaching solution agitated in a Waring blender fitted with a cooling jacket. By this means the yields of aminoquinoxalines obtained from 2-quinoxalinecarboxamide and its 6-chloro and 7-chloro derivatives were 97, 11, and 83%, respectively.

The two target chloroaminoquinoxalines possessed virtually the same ultraviolet absorption spectra and melting points (*ca.* 220°), in contrast to the significantly lower melting points (*ca.* 200°) earlier reported.[2,3] The infrared spectra of the two compounds, 2-amino-6- and -7-chloroquinoxalines, reported in this paper were different.

The accuracy of the structural proofs provided by these synthetic sequences was further demonstrated by transforming the aminochloroquinoxalines, *via* their diazonium salts, into the corresponding known[4] chloroquinoxalinones.

Experimental Section[5]

6-Chloro-2-quinoxalinecarboxamide.—A suspension of 6.7 g (0.03 mol) of 6-chloro-2-carbomethoxyquinoxaline[1] in 600 ml of concentrated ammonium hydroxide was shaken for 140 hr at 24° to give 4.9 g (80%) of amide, mp 299–300°. Three recrystallizations from dioxane (120 ml/g) gave 4.7 g (76%) of white needles: mp 300–301° sub; uv max 245 mμ (ε 41,200), 320 (7000), 331 (9000).

Anal. Calcd for $C_9H_6ClN_3O$: C, 52.07; H, 2.91; N, 20.24. Found: C, 51.80; H, 2.72; N, 20.51.

This material was also prepared (97%) by ammonolysis of 6-chloro-2-quinoxaloyl chloride.[1]

7-Chloro-2-quinoxalinecarboxamide.—The yield was 84%, from ethanol (200 ml/g): mp 259.5–260.5° sub; uv max 210 mμ (ε 28,300), 243 (44,700), 322 (inflection), 333 (6300).

Anal. Calcd for $C_9H_6ClN_3O$: C, 52.07; H, 2.91; N, 20.24. Found: C, 51.76; H, 2.99; N, 20.22.

2-Amino-6-chloroquinoxaline.—In a 1-qt Waring blender container (fitted with a 2-qt plastic pail serving as a jacket holding crushed ice) was placed 100 g of ice, 14.5 g of Clorox, (5.25% sodium hypochlorite), 5 ml of 6 *N* sodium hydroxide, and 30 ml of ice water. After stirring the mixture for 30 sec to the consistency of a frappé, 2.08 g (0.01 mol) of 6-chloro-2-quinoxalinecarboxamide was added in one portion. The mixture was stirred for 60 min, keeping the outside of the blender cool with crushed ice; the internal temperature of the mixture remained at 33°. The ice was removed from the cooling jacket, while stirring was continued for 1 hr; during this time the temperature of the reaction mixture was 81°.

The suspension was rinsed into a flask and heated to boiling, after which the reaction mixture was acidified with 30 ml of 6 *N* hydrochloric acid. After treatment with decolorizing carbon, filtration, and concentration to a volume of 50 ml, the solution was basified with 6 *N* sodium hydroxide. After 12 hr at 10°, filtration gave 0.2 g (11%) of pink solid, mp 220° sub. Recrystallization from ethanol (25 ml/g) gave 0.1 g (5.5%) of 2-amino-6-chloroquinoxaline: mp 220–221° sub; uv max 209 mμ (ε 42,200), 244 (35,500); ir 545 (CCl), 403 cm^{-1} (aromatic). Starting material (66%) was recovered from the reaction mixture.

Anal. Calcd for $C_8H_6ClN_3$: C, 53.50; H, 3.37; N, 23.40. Found: C, 53.79; H, 3.46; N, 23.54.

2-Amino-7-chloroquinoxaline.—The yield was 83%, from ethanol (20 ml/g): mp 219–220.5° sub; uv max 212 mμ (ε 42,900), 246 (33,100); ir 593 (CCl), 428 cm^{-1} (aromatic).

Anal. Calcd for $C_8H_6ClN_3$: C, 53.50; H, 3.37; N, 23.40. Found: C, 53.76. H, 3.52; N, 23.49.

Only in the far-infrared region of the infrared spectra were markedly different absorptions evident for the above compounds. The mixture (1:1) melting point of the two pure chloroaminoquinoxalines was 201–203° sub (lit.[2] mp 197–200°, referred to as the 6- or 7-chloro isomer; lit.[3] mp 199–200°, referred to as the 7-chloro isomer).

The reported[2,3] syntheses of 2-amino-6- (or 7-) chloroquinoxalines were repeated several times in this laboratory, mp 199–202° sub;[6] the materials obtained exhibited in all instances all four of the distinguishing infrared absorption peaks referred to above.

2-Quinoxalinone.—To a stirred solution (suspensions of the chloro-substituted quinoxalines) of 1.45 g (0.01 mol) of 2-aminoquinoxaline and 3 ml of acetic acid in 50 ml of water at 85° was added over 15 min a solution of 2 g of sodium nitrite in 33 ml of water. After 1 hr more of heating, gas evolution ceased; cooling in an ice bath precipitated 0.94 g (64%), mp 245–255°, of yellow 2-quinoxalinone. A solution of the product in 22 ml of 3 *N* sodium hydroxide was decolorized, clarified, and filtered. Acidification of the filtrate gave 0.82 g (56%) of product, mp 251–267°. Sublimation (200°, 4 mm) gave 0.57 g of 2-quinoxalinone, mp 269–270° dec (lit. mp 271°,[7] 265°,[8] 269°[9]). The H nmr spectra (10% w/w, 1 *N* sodium hydroxide) of this sample and of a commercial sample of 2-quinoxalinone were identical. This general procedure was used for the preparation of the chloro-substituted quinoxalinones.

6-Chloro-2-quinoxalinone.—The yield was 67%, from ethyl carbitol (25 ml/g): mp 312–313° dec, sub (lit. mp 305°,[4] 300–305°[8]); uv max 237 mμ (ε 37,800), 277 (4700), 344 (5400); uv max (0.1 *N* NaOH) 241 mμ (ε 34,600), 358 (7000) [lit.[3] uv max (0.1 *N* NaOH) 240 mμ (ε 26,100), 353 (7550)].

Anal. Calcd for $C_8H_5ClN_2O$: C, 53.21; H, 2.79; N, 15.51. Found: C, 53.47; H, 2.79; N, 15.78.

7-Chloro-2-quinoxalinone.—The yield was 68%, from ethyl carbitol (30 ml/g): mp 269–270° dec, sub (lit.[4] mp 270°); mmp (with 6-chloro-2-quinoxalinone) mp 240–255° dec, sub;

(3) H. G. Petering and G. J. Van Giessen, *J. Org. Chem.*, **26**, 2818 (1961).

(4) A. F. Crowther, F. H. S. Curd, D. G. Davey, and G. J. Stacey, *J. Chem. Soc.*, 1260 (1949).

(5) Spectra were recorded as follows: ir, Beckman IR-10, in KBr pellets; uv, Bausch and Lomb 505 or Jasco ORD/UV-5, in 95% ethanol, except where noted differently; H nmr, Hitachi Perkin-Elmer R-20, 60 MHz, 34°. Melting points, determined on a Thomas-Hoover apparatus, were uncorrected. Elemental analyses were performed by PCR, Inc., Gainesville, Fla.

(6) Petering and Van Giessen[3] asserted that pure 2-amino-7-chloroquinoxaline was obtained by hydrolysis of their 2-chloroalloxazine, III, obtained by condensation of 4-chloro-*o*-phenylenediamine with alloxan monohydrate in an appropriatel ' buffered solution. Wolf, *et al.*,[2] stated that only one isomer (not identified) was obtained by cleavage of their 7- (or 8-) chloroalloxazine.

(7) A. H. Gowenlock, G. T. Newbold, and F. S. Spring, *J. Chem. Soc.*, 622 (1945).

(8) O. Hinsberg, *Justus Liebigs Ann. Chem.*, **292**, 245 (1896).

(9) S. Motylewski, *Ber.*, **41**, 800 (1908).

uv max 206 mμ (ε 37,500), 232 (22,600), 285 (12,200), 334 (6900), 344 (7200); uv max (0.1 *N* NaOH) 240 mμ (ε 34,600), 349 (8900).

Registry No.—6-chloro-2-quinoxaline carboxamide, 27925-23-1; 7-chloro-2-quinoxaline carboxamide, 27925-24-2; 2-amino-6-chloroquinoxaline, 6726-76-7; 2-amino-7-chloroquinoxaline, 2427-70-5; 6-chloro-2-quinoxalinone, 27925-27-5; 7-chloro-2-quinoxalinone, 27925-28-6.

On the Transmission of Polar Effects by the Amide Moiety

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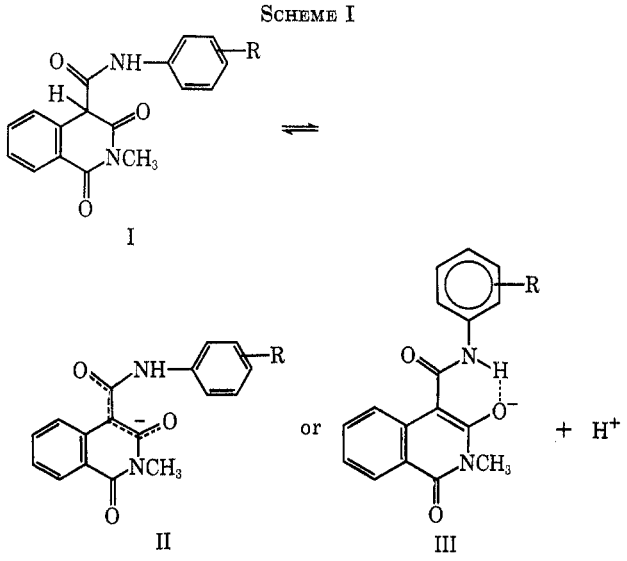
Recent, conflicting reports[1,2] concerning the proficiency of the amide group in transmitting electronic effects based on amide resonance contributions[3] prompt us to describe our results in this area.

Treatment of 2-methylisoquinoline-1,3(2*H*,4*H*)-dione with aryl isocyanates leads to 2-methyl-1,3(2*H*,4*H*)-dioxoisoquinoline-4-carboxanilides (I).[4,5] These compounds, which also may be prepared by the aminolysis of ethyl 2-methyl-1,3(2*H*,4*H*)-dioxoisoquinoline-4-carboxylate with appropriate anilines,[5] display acidic properties involving a keto–enolate anion equilibrium (Scheme I) to which the enol tautomer makes little or no contribution.[5]

SCHEME I



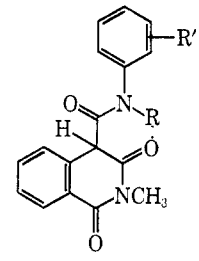
I II III

When the pK_a' values of anilides **1–13** (Table I) are plotted against the pK_a values of the correspondingly substituted anilines,[6] the equation for the resulting linear correlation is

$$pK_{a'_{anilide}} = 3.54 + 0.46\,pK_{a_{aniline}} \pm 0.155 \text{ (95\% confidence)} \quad (r = 0.968,\ n = 13) \quad (1)$$

TABLE I

PHYSICAL PROPERTIES AND METHODS OF PREPARATION OF 2-METHYL-1,3(2*H*,4*H*)-DIOXOISOQUINOLINE-4-CARBOXANILIDES[a]



Compd	R	R′	pK_a'	Mp, °C	Method of prepn	Solvent of recrystn
1	H	H	5.68	243–244 dec	*b*	CH_3CN
2	H	3-CH_3	5.72	224–225 dec	A[c]	CH_3CN
3	H	4-CH_3	5.85	232–234 dec	A	CH_3CN
4	H	3-OCH_3	5.60	206–207 dec	B[c]	CH_3CN
5	H	4-OCH_3	5.90	222–224	A	CH_3CN
6	H	4-OEt	5.96	210–211 dec	A	CH_3CN
7	H	3-F	5.21	217 dec	B	CH_3CN
8	H	4-F	5.60	222–224 dec	B	EtOAc
9	H	3-Cl	5.22	206–208	A	CH_3CN
10	H	4-Cl	5.20	213–214 dec	A	CH_3CN
11	H	4-Br	5.32	228–229 dec	B	CH_3CN
12	H	3-CF_3	5.05	188–190 dec	B	C_6H_6
13	H	3-$COCH_3$	5.23	177–178 dec	B	CH_3CN
14	H	4-COOEt	4.98	229–230 dec	B	CH_3CN
15	H	4-CF_3	4.94	210–211 dec	B	CH_3CN
16	H	4-SO_2NH_2	4.91	231–232 dec	B	CH_3CN
17	CH_3	H	7.57	160–162	*b*	C_6H_6–C_6H_{14}

[a] All analyses are within ±0.3% of calculated values. [b] See ref 5. [c] See Experimental Section.

The data for the *p*-carbethoxy-, *p*-trifluoromethyl-, and *p*-sulfamoylanilide–aniline pairs (Table I, no. **14–16**) do not fit this relationship and have not been included in calculating eq 1.

A Hammett plot of the same data (Figure 1)[7] yields a ρ value of 1.25. Significantly, the *p*-carbethoxy, *p*-trifluoromethyl, and *p*-sulfamoyl groups are included in this correlation; however, this is true only when their σ values, and not when their σ^- values, are utilized. This, together with the failure of these pairs to fit eq 1, indicates that polar effects are transmitted to the amide linkage but effects which depend upon direct resonance interaction of the anilide nitrogen with the substituent group are only slightly, if at all, so transmitted.

These Hammett results are in general agreement with those of Johnson and coworkers[1] who found a ρ value of 1.77 in their study of the kinetics of ethanol addition to substituted acrylanilides. The failure of Donohue and coworkers[2] to obtain a significant ρ value in correlating the pK_a values of various 4-substituted 4′-aminobenzanilides with σ may reflect the fact that the substituents in their system were not on the ring bearing the anilide nitrogen. In the present system, as well as in that of the acrylanilide study,[1] the substituents are located on the anilide moiety.

The question of whether the primary effect of the substituents (Scheme I) is directed at the capacity of the anilide carbonyl functionality to stabilize the enolate anion (II) or at the ability of the hydrogen on the anilide nitrogen to bond to the enolate anion

(1) H. W. Johnson, Jr., E. Ngo, and V. A. Pena, *J. Org. Chem.*, **34**, 3271 (1969).
(2) J. A. Donohue, R. M. Scott, and F. M. Menger, *ibid.*, **35**, 2035 (1970).
(3) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 281.
(4) S. B. Kadin and E. H. Wiseman, *Nature*, **222**, 275 (1969).
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(7) σ values are from the compilation of D. H. McDaniel and H. C. Brown, *J. Org. Chem.* **23**, 420 (1958), except for the value of the *p*-fluoro substituent which is from A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 388 (1961).