

Figure 2. Variation of  $K_{\rm H}/K_n$  with *n* for 2-naphthol in the ground state.

from this theory is now usually called the "Gross-Butler equation," which may be written

$$\frac{K_{\rm H}}{K_{\rm n}} = \frac{1 - n + n\phi}{(1 - n + nl)^3}$$
  
$$\phi = l^3(K_{\rm H}/K_{\rm D})$$
(5)

where  $K_n$  is the acidity constant in a water-heavy water solvent mixture of *n* atom fraction deuterium, and *l* is a parameter, usually assumed to equal 0.67.<sup>13,18</sup> Genenerally, the Gross-Butler equation fits experimental data very well for weak, monobasic acids; more refined equations must be used for strong acids.<sup>13,19</sup>

(18) A. J. Kresge and A. L. Allred, J. Am. Chem. Soc., 85, 1541 (1963).



Figure 3. Variation of  $K_{\rm H}/K_n$  with *n* for 2-naphthol in the first excited singlet state.

In the present study, the variation of  $K_{\rm H}/K_n$  was measured as a function of n for 2-naphthol in its ground and first excited singlet states; the experimental results are compared with the curves predicted from the Gross-Butler equation in Figures 2 and 3. Agreement between theory and experiment is excellent for the ground state, and, considering the uncertainties involved in measuring excited-state acidities, the agreement is surprisingly good for the first excited singlet. To a first approximation, it is concluded that the Gross-Butler equation adequately predicts  $pK_n$  values in mixed  $D_2O-H_2O$  solvents, provided that  $pK_{H}^*$  is fairly large. This observation lends further support to the observation that magnitudes of equilibrium isotope effects in electronically excited aromatic compounds can be predicted, with a surprising degree of accuracy, from ground-state equations and parameters.

(19) E. L. Purlee, *ibid.*, **81**, 263 (1959); V. Gold, *Trans. Faraday* Soc., 56, 255 (1960).

# Substituent Effects. V.<sup>1,2</sup> Further Evidence Concerning the Nature of the Inductive Effect

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Abstract: The ultraviolet absorption spectra of *m*- and *p*-aminophenyltrimethylammonium ions, of *m*- and *p*-trifluoromethylaniline, and of  $\beta$ - and  $\gamma$ -aminopyridine have been compared with that of aniline; the results suggest that the "inductive" substituent CF<sub>3</sub> operates mainly by a field effect rather than by a  $\pi$ -inductive effect. This conclusion was also supported by comparisons of the proton n.m.r. spectra of *p*-tolyl- and *p*-methylbenzyl-trimethylammonium ions, of *p*-trifluoromethyltoluene, and of  $\gamma$ -picoline in various solvents.

There are a number of different ways in which a substituent can influence a distant reaction center; the purpose of the work described in this series of papers

(3) N.A.S.A. Predoctoral Fellow, 1962–1964; National Institutes of Health Predoctoral Fellow, 1964–1965.

is to assess the relative importance of the possible modes of action of substituents, and to establish some procedure for estimating the effects of given substituents in arbitrary molecules. The first four papers of this series described a study of substituent effects in naphthalene; in them it was concluded that the so-called "inductive effect" of classical organic theory is in fact a direct field

<sup>(1)</sup> This work was supported by the Army Research Office through Grant DA-ARO-D-31-124-G496.

<sup>(2)</sup> Part IV: M. J. S. Dewar and P. J. Grisdale, J. Am. Chem. Soc., 84, 3548 (1962).

When an atom forms a polar bond, it acquires<sup>4</sup> a formal charge; this must affect its electronegativity and so lead to an induced polarization of other bonds formed by it. The induced polarization of adjacent  $\sigma$ bonds corresponds to the classical inductive ( $\sigma$ -inductive) effect; if the atom in question forms part of a conjugated system, one would also anticipate an analogous polarization of the  $\pi$  electrons, and there is evidence<sup>5</sup> that this inductoelectromeric<sup>5</sup> or  $\pi$ -inductive<sup>6</sup> effect can be important in certain cases. Indeed, since  $\pi$ electrons are more polarizable than  $\sigma$  electrons, one might expect the importance of the inductive effect relative to that of the field effect to be greater in  $\pi$ systems; it therefore seemed to us that an obvious first step would be a study of the relative importance of  $\pi$ inductive and field effects in such a case.

Replacement of a carbon atom in a conjugated system by nitrogen leads to a polarization of the  $\pi$  electrons, due to the greater electronegativity of nitrogen; the effects of such a replacement should therefore show the consequences of a change in electronegativity of a given atom in a conjugated system. Conversely one might expect the dominant effect of a charged substituent  $(X^+)$  to be by the field effect; for, as Kirkwood and Westheimer<sup>7</sup> first demonstrated, the effects of charged substituents can be explained quantitatively on the assumption that they act only in this way. Consider then a conjugated system R=CH-S. Comparison of its properties with those of R=N-S will show the qualitative consequences of altering the electronegativity of one atom in it, while comparison with  $R = C(X^+) - S$ should indicate the consequences of introducing a substituent that acts primarily by the field effect. Comparison of these extremes with the behavior of a comparison R = C(Y) - S, where Y is a neutral "inductive" substituent, should then indicate the relative importance of the field and inductive effects in the latter case. This argument of course assumes that there is a marked difference between the two reference systems, and that the groups = N- and = C(X+)- do differ in their electronic effects. However a difference in behavior between the two reference systems would be an automatic indication that the second condition is being met. Since the effect of the grouping =N- in a conjugated system is due almost entirely to a direct polarization of the  $\pi$  electrons by the electronegative nitrogen atom, such a difference in behavior would confirm the assumption that a positively charged group  $X^+$  should act at least to a large extent by some process other than the  $\pi$ -inductive effect.

In this work we studied the effects of such structural changes on two properties of benzene derivatives;

(7) J. G. Kirkwood and F. H. Westheimer, J. Chem. Phys., 6, 506 (1938); F. H. Westheimer and J. G. Kirkwood, *ibid.*, 6, 513 (1938).

first, the frequency of the first transition in aniline, and second, the proton n.m.r. chemical shifts in toluene. For the charged group  $X^+$  we used Me<sub>3</sub>N<sup>+</sup>; for Y we used F<sub>3</sub>C, a group known to exert, in classical terminology, a large positive inductive effect.<sup>8</sup> Thus, the compounds studied were the following.



### **Procedure and Results**

All of these were known compounds except VIb; this was obtained from *p*-trifluoromethylphenylmagnesium bromide and methyl iodide. The aminophenyltrimethylammonium salts IVa and Va have been prepared by Roberts, Clement, and Drysdale<sup>10</sup> by reduction of the corresponding nitro compounds; we prepared them more conveniently by quaternizing *m*-acetamido- or *p*benzamidodimethylaniline and hydrolyzing the resulting acylaminophenyltrimethylammonium salts.

The ultraviolet spectra of compounds I, II, IV, and V, and of aniline, were measured at 27° in buffered aqueous solution (pH 10.0) with a Beckman DK2 recording spectrophotometer. The proton n.m.r. spectra of compounds III and VI were measured in nitromethane or deuterium oxide with a Varian A-60 spectrometer, using tetramethylsilane (in CH<sub>3</sub>NO<sub>2</sub>) or sodium 3-trimethylsilylpropane-1-sulfonate (in D<sub>2</sub>O) as internal standards. In the latter case the chemical shifts ( $\tau'$  scale) were corrected to the  $\tau$  scale by comparison of published data<sup>11</sup> for acetone, acetonitrile, and dioxane; these lead to the relation

$$\tau = \tau' + 0.13 \pm 0.04 \text{ p.p.m.}$$
 (1)

The  $\tau$  scale is defined here for chemical shifts in carbon tetrachloride; to compare the effects of carbon tetrachloride and nitromethane, we measured the n.m.r. spectrum of dioxane in nitromethane against tetramethylsilane as internal standard. The value found ( $\tau$  6.42) agreed within the limits of experimental error

(8) Recently Sheppard<sup>9</sup> has claimed that  $F_3C$  can exert a -E effect directed mainly into the *meta* position of benzene by interaction of unshared electrons of the fluorine atoms with the  $\pi$  electrons of the ring. This idea seems to us quite unacceptable, for three reasons. First, there is no analogy suggesting that interactions of this kind can be significant. Second, there is no analogy for a resonance effect directed specifically into the *meta* positions. Third, the evidence quoted by Sheppard can be explained without difficulty in terms of a normal  $\pi$ -inductive effect; in the case of *p*-fluorobenzotrifluoride, this would lead to mutual conjugation<sup>5</sup> and so to an enhanced deshielding of the ring fluorine.

(9) W. A. Sheppard, J. Am. Chem. Soc., 87, 2410 (1965).

(10) J. D. Roberts, R. A. Clement, and J. J. Drysdale, *ibid.*, 73, 2181 (1951).
(11) R. J. Abraham and W. A. Thomas, J. Chem. Soc., 3739 (1964).

<sup>(4)</sup> Throughout this paper we will be using the localized bond model for  $\sigma$  bonds; for discussions concerning the justifiability of this see M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962; *Tetrahedron Suppl.*, **19** (2), 89 (1963); *Chem. Eng. News*, **43** (2), 86 (1965).

<sup>(5)</sup> D. A. Brown and M. J. S. Dewar, J. Chem. Soc., 2406 (1953);
M. J. S. Dewar, J. Am. Chem. Soc., 74, 3357 (1952).
(6) H. H. Jaffé, J. Chem. Phys., 20, 279, 778 (1952); J. Am. Chem.

<sup>(6)</sup> H. H. Jaffe, J. Chem. Phys., 20, 279, 778 (1952); J. Am. Chem. Soc., 76, 4261, 5843 (1954); 77, 274 (1955).

with that<sup>11</sup> ( $\tau$  6.43) for dioxane in carbon tetrachloride. The effect of changing from nitromethane to carbon tetrachloride as solvent therefore seems to be negligible.

The first three columns of Table I list wave lengths and transition energies for the lowest transitions of aniline and of compounds I, II, IV, and V. Table II shows the proton n.m.r. chemical shifts ( $\tau$  scale) for toluene, and for compounds III and VI, using the numbering indicated above; the  $J_{23}$  coupling constants are also listed.

Table I.	Wave Ler	igths and	Transition	Energies	for the
Lowest Tr	ransitions (	of Aniline	e Derivative	s and Am	inopyridines

	λ		Transition energy		
Compd.	mμ	Log e	Obsd.	Calcd.	
Aniline	278	3.17	4.48	4.37	
I	288	3.49	4.31	4.37	
II	265ª	Ca. 3.34	4.68	4.75	
IVa	283	3.36	4.39	4.32	
Va	280	3.16	4.43	3.70	
IVb	288	3.19	4.31		
Vb	275ª	3.12	4.52		

<sup>a</sup> Shoulder.

Table II. Proton N.m.r. Spectra of Substituted Toluenes

in VIa, 2.20 in VIc, and 2.33 in VIb. In  $\gamma$ -picoline (III) on the other hand there is a much larger shift to low field for the  $\alpha$  protons, while the  $\beta$  protons show no significant shift in either direction. On this basis one can conclude immediately that the group CF<sub>3</sub> acts predominantly by a field effect rather than by a  $\pi$ -inductive effect. The same conclusion follows, though less spectacularly, from the chemical shifts for the methyl protons; the differences from toluene are much greater in VIb and VIa than in III, and the value for VIc indicates that the effect of trifluoromethyl is much closer to that of Me<sub>3</sub>N<sup>+</sup>, or Me<sub>3</sub>N<sup>+</sup>CH<sub>2</sub>, than that of a ring nitrogen.

This argument rests of course on the assumption that the group  $N^+Me_3$  acts mainly by a field effect; the results in Table II are certainly consistent with this. Thus since an inductive effect is usually considered to depend simply on the number of bonds through which it is transmitted, one might expect the effects of  $Me_3N^+$ to be the same in the 3-position of VIc and in the 2position of VIa. This is not the case. More striking still is the effect of changing the solvent from nitromethane to deuterium oxide. If the chemical shifts were due to inductive effects, one would not expect this

Compd.	Solvent	Internal std. <sup>a</sup>	$\mathrm{H}_{2},^{b}_{ au}$	${f H_3},^b_ au$	$(H_2 - H_3)$	J <sub>23</sub> , c.p.s.	$\mathbf{H}_{7},^{b}$
VId	CH <sub>3</sub> NO <sub>2</sub>	TMS	2.98	2.98	0		7.73
III	$CH_3NO_2$	TMS	2.88	1.60	1.28	6	7.70
VIb	$CH_3NO_2$	TMS	2.69	2.45	0.23	8	7.62
VIa	CH <sub>3</sub> NO <sub>2</sub>	TMS	2.58	2.15	0.43	9	7 62
	$D_2O$	TSPS	2.58	2.26	0.32	9	7.62
VIc	CH <sub>3</sub> NO <sub>2</sub>	TMS	2.67	2.44	0.23	8	7.59
	$D_2O$	TSPS	2.65	2.65	0.00		7.59

<sup>a</sup> TMS = tetramethylsilane; TSPS = sodium 1-trimethylsilylpropane-3-sulfonate. <sup>b</sup> For numbering see formulas in text.

## Discussion

Compounds III and VI can be regarded as 4-substituted toluenes; the effect of the substituent therefore should be measured by the chemical shifts relative to those of the ring protons in toluene. The ring protons in toluene form an A<sub>2</sub>B<sub>2</sub>C system; fortunately, however, the chemical shifts are all identical so that only a single line is observed in the n.m.r. spectrum at  $\tau$  2.87 (in nitromethane). The chemical shifts in nitromethane, relative to toluene, are then as follows.



Cursory inspection of these results indicates that  $CF_3$  behaves exactly like the charged groups, and entirely differently from ring nitrogen; in the former cases all four ring protons show a large shift to lower field, the ratio of the shifts for the 3- and 2-protons being 2.50

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change to have any large effect. In fact the shifts due to a charged substituent ( $Me_3N^+$  or  $CH_2N^+Me_3$ ) are much smaller in  $D_2O$  than in  $CH_3NO_2$ , and the differences between the 3- and 2-protons also decrease; indeed, with VIc the difference vanishes.

Both these results would be expected if  $Me_3N^+$  acts primarily by a field effect. Thus the distance from nitrogen to a 2-position in VIa is greater than the mean distance (assuming free rotation) from nitrogen to a 3-position in VIc, and the electrostatic field at the ring carbon therefore should be less in the former case. The effect of solvent is of course immediately intelligible in terms of a field effect, for replacing nitromethane by the more polar deuterium oxide would be expected both to reduce the magnitudes of the chemical shifts and also to decrease the differences between those for the 3- and 2-positions.

Incidentally it is interesting that the ratio of chemical shifts for the 3- and 2-positions in nitromethane is less for VIc (2.20) than for VIa (2.50); this again would be expected if a field effect is operating, for the mean distances to nitrogen are more nearly similar in VIc than in VIa.

Proton n.m.r. chemical shifts reflect the structures of ground states of molecules; the spectral differences in Table I on the other hand probably refer mainly to the effects of structural changes on the relative energies of excited states. Here again CF<sub>3</sub> seems to act mainly by a field effect, although the distinction is less clear. Thus while the spectra of the two *para*-substituted anilines, Va and Vb, closely resemble that of aniline itself, the first absorption band of  $\gamma$ -aminopyridine (II) appears at much shorter wave lengths. In this case, however, there is a clear indication that the trifluoromethyl group does also show a significant  $\pi$ -inductive effect. Thus while *p*-Me<sub>3</sub>N<sup>+</sup> has a small bathochromic effect, the effect of CF<sub>3</sub>, while also small, is hypsochromic. Moreover the bathochromic effect of *m*-CF<sub>3</sub> is much greater than that of *m*-Me<sub>3</sub>N<sup>+</sup>, the spectral shift being identical with that observed in  $\beta$ -picoline (I). If we write the effect of CF<sub>3</sub> in the form

(effect of 
$$CF_3$$
) =  $a$ (effect of  $Me_3N^+$ ) +

$$b$$
(effect of pyridine N) (2)

we can solve for a and b using the data in Table I; we find

$$a = 1.03; b = 0.46$$
 (3)

The effect of  $CF_3$  therefore resembles more closely that of  $Me_3N^+$  than that of introducing a nitrogen atom into the ring.

These arguments rest on our conclusion that the spectrum of aniline is affected in different ways by changing the electronegativity of a ring atom, and by introducing a positive charge at a position adjacent to the ring. We therefore carried out some MO calculations to see if they would support this deduction from the observed spectra.

The calculations were carried out by a simple modification of the Pople SCF method.<sup>12</sup> The parameters used were as follows.

amine nitrogen

 $Z = 4.80; W_{\rm N} = W_{\rm C} - 17.37 \text{ e.v.}; (ii,ii) = 16.57 \text{ e.v.}$ 

ring nitrogen

 $Z = 3.57; W_{\rm N} = W_{\rm C} - 2.96 \text{ e.v.}; (ii,ii) = 12.34 \text{ e.v.}$ 

resonance integrals

for ring bonds, 
$$-2.281 \text{ e.v.}$$
; for CNH<sub>2</sub>,  $-1.500 \text{ e.v.}$  (4)

The remaining repulsion integrals were calculated by the uniformly charged sphere method, using "upperlower" values; these correspond closely to those given by the Pariser-Parr approximation.<sup>13</sup> The parameter values in eq. 4 correspond closely to those suggested by recent work in these laboratories.<sup>14</sup> In calculating excitation energies, it is necessary to introduce at least a limited amount of configuration interaction. Following an argument put forward by Dewar and Longuet-Higgins<sup>15</sup> we decided to include configuration interaction between the first four excited states. This procedure was used to estimate excitation energies for aniline, and for  $\beta$ - and  $\gamma$ -aminopyridine. In order to treat the anilinium ions IVa and Va, we needed to include the electrostatic interactions of a charge adjacent to the ring. This was done by treating the charge on the Me<sub>3</sub>N<sup>+</sup> group as a point charge +e located at the nucleus of the nitrogen atom; the valence-state ionization potentials of the various atoms in the aniline system were then corrected for the electrostatic effect of this charge, using the uniformly charged sphere approximation. Thus, the corrected valence state ionization potential of atom i ( $W_i$ ) was given in terms of the value in aniline ( $W_i$ ) by

$$W_{i}' = W_{i} - e^{2}(r_{i}^{2} + R^{2})^{-1/2}/D$$
 (5)

where  $r_i$  is the internuclear distance between atom i and the exocyclic charge, R is the radius of the sphere used to approximate one lobe of the 2p orbital of atom i, and Dis the effective dielectric constant. After some experiment, we set D = 10. The results of these calculations are shown in Table I in the last column.

The calculated excitation energies agree qualitatively with our expectations in that they predict a hypsochromic shift on passing from  $\beta$ - to  $\gamma$ -aminopyridine, but a bathochromic shift on passing from *m*- to *p*-aminophenyltrimethylammonium ion. The quantitative agreement is poor, but probably as good as could be expected; although the method used gives excellent results for heats of formation of molecules in their ground states, it would not be expected to give accurate values for excitation energies. Moreover the treatment of the surrounding medium as a continuous dielectric with uniform dielectric constant *D* is clearly a gross approximation.

#### Conclusions

Branch and Calvin<sup>16</sup> first tried to account quantitatively for the long-range influence of substituents in saturated systems in terms of a classical inductive effect propagated by successive polarization of bonds; they deduced that the fall-off factor, *i.e.*, the attenuation per bond, was approximately 1/2.8, and a number of other authors also have recommended similar values. The work described in the present series of papers suggests that this is much too large, and that the major longrange effect of "inductive" substituents is due to a direct electrostatic interaction across space rather than to the classical inductive effect. Several other authors recently have arrived at similar conclusions; for example, Holtz and Stock<sup>17</sup> have shown that the effects of dipolar substituents in bicyclooctanes can be accounted for quantitatively in terms of field effects; Spiesecke and Schneider<sup>18</sup> compared H<sup>1</sup> and C<sup>13</sup> chemical shifts in substituted benzenes and observed that the effects meta to substituents are very small, implying that inductive effects are negligible; and Hooper and Bray<sup>19</sup> found that substituents separated from a chlorine or bromine atom by three or more intervening carbon atoms have a negligible effect on the nuclear quadrupole resonance frequency of halogen, again indicating that inductive effects die away rapidly along a carbon chain.

Our results also suggest that  $\pi$ -inductive effects may be more important in excited states of molecules than

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<sup>(18)</sup> H. Spiesecke and W. G. Schneider, J. Chem. Phys., 35, 731 (1961).

<sup>(19)</sup> H. O. Hooper and P. J. Bray, ibid., 33, 334 (1960).

in their ground states; this of course would be expected.<sup>4</sup> Bond localization is a phenomenon associated with closed-shell structures; resonance interactions in general, and  $\pi$ -inductive effects, in particular, should therefore be more important in open-shell systems such as excited states.

## **Experimental Section**

Melting points are corrected (Fisher-Johns Block).

 $\gamma$ -Aminopyridine. A commercial sample was recrystallized from benzene-chloroform, m.p. 159-161° (lit. 20 m.p. 158°).

m-Acetylaminophenyltrimethylammonium iodide. Acetylation of m-dimethylaminoaniline (5.0 g.) with acetic anhydride (10 ml.) gave m-acetylaminodimethylaniline (m.p. 85.5-86.5°; lit.<sup>21</sup> m.p. 87°) which was boiled overnight under reflux with excess methyl iodide, giving m-acetylaminophenyltrimethylammonium iodide (6.35 g., 87% over-all) which crystallized from absolute methanol in pale yellow needles, m.p. 217.5–218°. Anal. Calcd. for  $C_{11}H_{17}$ -IN2O: C, 41.26; H, 5.35; I, 39.64; N, 8.75. Found: C, 41.42; H, 5.63; I, 39.41; N, 8.54.

m-Aminophenyltrimethylammonium Chloride Hydrochloride. An aqueous ethanolic solution of m-acetylaminophenyltrimethylammonium iodide (3.0 g.) was treated with silver oxide (10 g.) and filtered, and the filtrate was made strongly acid with hydrochloric acid and refluxed overnight. After evaporation in vacuo, the residue crystallized from methanol-ether as colorless plates, transition at 165°, m.p. 182–186° (lit. m.p. 185–189°). Anal. Calcd. for  $C_9H_{16}Cl_2N_2$ : C, 48.44; H, 7.23; Cl, 31.73; N, 12.55. Found: C, 48.50; H, 7.19; Cl, 31.75; N, 12.46.

p-Benzoylaminophenyltrimethylammonium Iodide. An ethereal solution of p-benzoylaminodimethylaniline<sup>22</sup> (2.50 g.) and excess methyl iodide was boiled overnight under reflux. The precipitate was recrystallized twice from methanol, giving p-benzoylaminophenyltrimethylammonium iodide (2.85 g., 72%) as colorless needles, which began to melt at 211°, resolidified, and then melted sharply at 232-234°. Anal. Calcd. for C16H19IN2O: C, 50.27; H, 5.01; I, 33.20; N, 7.33. Found: C, 50.26; H, 4.83; I, 33.45; N, 7.47.

p-Aminophenyltrimethylammonium Chloride Hydrochloride. The above iodide (2.85 g.) was boiled for 1 hr. under reflux with excess aqueous ethanolic hydrochloric acid, the solution was evaporated to dryness, the residue was taken up in absolute methanol and precipitated with ether, and the precipitate was extracted with boiling benzene. The residue (1.50 g.) was shaken with a suspension of silver oxide (5 g.) in aqueous ethanol and filtered, and the filtrate was made strongly acid with hydrochloric acid and evaporated to dryness. Repeated crystallization of the residue from methanol-ether gave p-aminophenyltrimethylammonium chloride (0.60 g.), m.p. 211° dec. (lit. m.p. 206-206.5, <sup>10</sup> 219°<sup>23</sup>). Anal. Calcd. for  $C_9H_{16}Cl_2N_2$ : C, 48.44; H, 7.23; Cl, 31.78; N, 12.55. Found: C, 48.33; H, 7.52; Cl, 31.76; N, 12.45.

p-Tolyltrimethylammonium Iodide. Prepared from methyl iodide and from N,N-dimethyl-p-toluidine, the iodide had m.p. 218-219° (lit.<sup>24</sup> m.p. 222°).

p-Methylbenzyltrimethylammonium Iodide. Reaction of pmethylbenzyl bromide with dimethylamine gave p-methylbenzyldimethylamine,  $n^{27}D$  1.4945 (lit.<sup>25</sup>  $n^{25}D$  1.499). The methiodide crystallized from methanol in colorless plates, m.p. 210-211.5° (lit.<sup>25</sup> m.p. 210–211°).

p-Methylbenzotrifluoride. A solution of methyl iodide (28.4 g.) in dry benzene (50 ml.) was added dropwise to a boiling ethereal solution of p-trifluoromethylphenylmagnesium bromide, prepared from p-bromobenzotrifluoride (14.3 g.) and magnesium (1.6 g.). After 24 hr. under reflux the cooled solution was treated with dilute sulfuric acid and the organic layer was distilled through a 24-in. spinning-band column, giving p-methylbenzotrifluoride (3.5 g., 34%) as a colorless liquid, b.p. 129°. A sample purified for analysis by gas-liquid chromatography on silicone gum rubber had n<sup>26</sup>D 1.4320. Anal. Calcd. for C<sub>8</sub>H<sub>7</sub>F<sub>3</sub>: C, 60.00; H, 4.41; mol. wt., 160. Found: C, 59.93; H, 4.68; mol. wt. (mass spectroscopy), 160. The mass spectrum also showed major peaks at mass number 91 ( $H_3CC_6H_4^+$ ) and 69 ( $F_3C^+$ ).

The remaining materials and solvents were commercial samples whose physical constants agreed with those reported in the literature.

- (24) G. R. Clemo and J. M. Smith, J. Chem. Soc., 2425 (1928).
   (25) E. L. Eliel, T. N. Ferdinand, and M. C. Herrmann, J. Org. Chem., 19, 1693 (1954).

# New Heteroaromatic Compounds. XXIV.<sup>1</sup> Bromination and Nitration of 4-Methyl-4,3-borazaroisoquinoline

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Abstract: Bromination or nitration of 4-methyl-4,3-borazaroisoquinoline<sup>3</sup> (Ib) gave the 8-bromo (IIa) and 8-nitro (IIb) derivatives as the sole isolable products. The theoretical implications of this, and of the proton n.m.r. spectra of Ib, IIa, and IIb, are discussed.

Previous papers of this series have described a series of novel heteroaromatic compounds containing boron, isoelectronic with normal aromatics and derived from them by replacing a pair of adjacent carbon atoms by boron and nitrogen. One of the more interesting systems of this kind is 4,3-borazaroisoquin-

(3) M. J. S. Dewar and R. C. Dougherty, J. Am. Chem. Soc., 86, 433 (1964).

oline (Ia), which is isoelectronic with isoquinoline; derivatives<sup>3</sup> of this showed unusual stability to hydrolysis and oxidation, even by comparison with other boron-containing heteroaromatics, and preliminary studies showed that they also underwent typical electrophilic substitution reactions. Reactions of this kind are of considerable theoretical interest, for the relationship between the reactivity of such a boroncontaining aromatic, and of the isoelectronic "normal" system from which it is derived, provides a good test

<sup>(20)</sup> B. Emmert and W. Dorn, Ber., 48, 491 (1915).
(21) W. Staedel and H. Bauer, *ibid.*, 19, 1945 (1886).

<sup>(22)</sup> E. Börnstein, ibid., 29, 1482 (1890).

<sup>(23)</sup> J. Pinnow and E. Koch, ibid., 30, 2860 (1897).

<sup>(1)</sup> Part XXIII: G. C. Culling, M. J. S. Dewar, and P. A. Marr, J. Am. Chem. Soc., 86, 1125 (1964). (2) Robert A. Welch Postdoctoral Fellow, 1964-1965.