

in their ground states; this of course would be expected.⁴ Bond localization is a phenomenon associated with closed-shell structures; resonance interactions in general, and π -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).

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

m-Acetylamino-phenyltrimethylammonium iodide. Acetylation of *m*-dimethylaminoaniline (5.0 g.) with acetic anhydride (10 ml.) gave *m*-acetylamino-dimethylaniline (m.p. 85.5–86.5°; lit.²¹ m.p. 87°) which was boiled overnight under reflux with excess methyl iodide, giving *m*-acetylamino-phenyltrimethylammonium iodide (6.35 g., 87% over-all) which crystallized from absolute methanol in pale yellow needles, m.p. 217.5–218°. *Anal.* Calcd. for C₁₁H₁₇IN₂O: 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*-acetylamino-phenyltrimethylammonium 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 C₉H₁₀Cl₂N₂: 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-Benzoylamino-phenyltrimethylammonium Iodide. An ethereal solution of *p*-benzoylamino-dimethylaniline²² (2.50 g.) and excess methyl iodide was boiled overnight under reflux. The precipitate was recrystallized twice from methanol, giving *p*-benzoylamino-phenyltrimethylammonium 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. 206–206.5,¹⁰ 219²³). *Anal.* Calcd. for C₉H₁₀Cl₂N₂: 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.²⁴ m.p. 222°).

p-Methylbenzyltrimethylammonium Iodide. Reaction of *p*-methylbenzyl bromide with dimethylamine gave *p*-methylbenzyl-dimethylamine, *n*²⁵_D 1.4945 (lit.²⁵ *n*²⁵_D 1.499). The methiodide crystallized from methanol in colorless plates, m.p. 210–211.5° (lit.²⁵ 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*²⁶_D 1.4320. *Anal.* Calcd. for C₈H₇F₃: 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 (H₃CC₆H₄⁺) and 69 (F₃C⁺).

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

(23) J. Pinnow and E. Koch, *ibid.*, **30**, 2860 (1897).

(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).

(20) B. Emmert and W. Dorn, *Ber.*, **48**, 491 (1915).

(21) W. Staedel and H. Bauer, *ibid.*, **19**, 1945 (1886).

(22) E. Börnstein, *ibid.*, **29**, 1482 (1890).

New Heteroaromatic Compounds. XXIV.¹ Bromination and Nitration of 4-Methyl-4,3-borazaroisoquinoline

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Contribution from the Department of Chemistry, The University of Texas, Austin, Texas 78712. Received September 7, 1965

Abstract: Bromination or nitration of 4-methyl-4,3-borazaroisoquinoline³ (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-

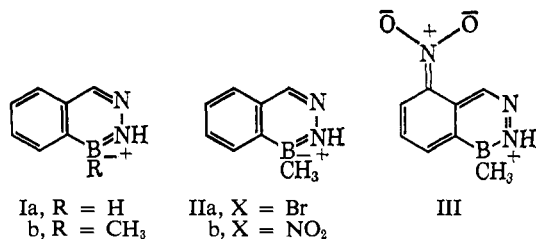
oline (Ia), which is isoelectronic with isoquinoline; derivatives³ of this showed unusual stability to hydrolysis and oxidation, even by comparison with other boron-containing heteroaromatics, and preliminary studies showed that they also underwent typical electrophilic substitution reactions. Reactions of this kind are of considerable theoretical interest, for the relationship between the reactivity of such a boron-containing aromatic, and of the isoelectronic "normal" system from which it is derived, provides a good test

(1) 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.

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

of chemical theory. We have therefore examined in detail various substitution reactions of 4-methyl-4,3-borazaroisoquinoline (Ib). The results, together with the proton n.m.r. spectra of these compounds, are discussed in terms of a recently developed SCF-MO treatment of conjugated systems.



When Ib was treated with 1 molar equiv. of bromine in acetic acid, a dark orange solid separated which, on treatment with water, gave 8-bromo-4-methyl-4,3-borazaroisoquinoline (IIa) in 84% yield. The structure of IIa was established by elemental analysis and oxidative degradation to *o*-bromobenzoic acid; no other isomer could be isolated from the reaction. The intermediate orange solid presumably was an adduct of Ib with HBr; the color, and the fact that IIa was not precipitated from acetic acid solution by dry hydrogen chloride, suggest that it probably was not a simple hydrobromide of IIa. It could perhaps have been the arenonium ion intermediate, with bromine and hydrogen attached at the 8-position; this would be expected to lose hydrogen bromide readily on treatment with water, giving IIa.

The nitration of 4-methyl-4,3-borazaroisoquinoline did not proceed as cleanly as did the bromination. Nitration with nitric acid in concentrated sulfuric acid gave a product which seemed to undergo autoxidation to form a nonvolatile material. The crude nitration product was insoluble in common nonpolar organic solvents but was soluble in polar ones such as acetone, trifluoroacetic acid, and dimethyl sulfoxide. Recrystallization of the product from a mixture of acetone and water gave, in about 30% yield, a compound which seemed to be 8-nitro-4-methyl-4,3-borazaroisoquinoline (IIb). The mass spectrum of the material showed a parent peak of *m/e* 189 and elemental analysis of a portion further purified by sublimation also was in excellent agreement with this formulation. The orientation of the nitro group followed from analogy with IIa and from the proton n.m.r. spectrum (see below). Decomposition accompanied the sublimation, and the sublimate also was found to leave a residue during the mass spectral analysis, a further indication of its instability.

The instability of the 8-nitro derivative (IIb) can be explained in terms of mutual conjugation between the imino and nitro groups; this could be expressed in resonance terminology in terms of a contribution by the dipolar resonance structure III. The enhanced polarity due to such a contribution would account for the fact that IIb dissolves only in polar solvents, while contributions by III also would tend to destabilize the boron-containing ring. Similar destabilizing effects by electromeric substituents have been noted in the 10,9-borazarophenanthrene series.⁴

(4) See M. J. S. Dewar and V. P. Kubba, *Tetrahedron*, **7**, 213 (1959); M. J. S. Dewar and P. M. Maitlis, *ibid.*, **15**, 35 (1961).

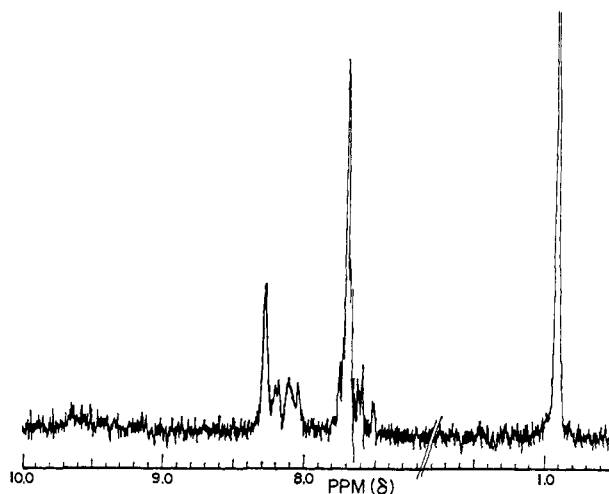


Figure 1. Proton n.m.r. spectrum of 4-methyl-4,3-borazaroisoquinoline in carbon tetrachloride.

Attempts to carry out the nitration with nitric acid in acetic anhydride yielded only small amounts of tar. Nitration of II with nitronium tetrafluoroborate in the manner described by Olah⁵ also failed to give nitration products, nearly all the starting material being recovered.

4-Methyl-4,3-borazaroisoquinoline also resisted acetylation by acetyl chloride in the presence of stannic chloride or aluminum chloride, unchanged starting material being recovered in each case.

It is well recognized that the deuteration of aromatic compounds by sulfuric acid-*d*₂ involves an electrophilic substitution. Several attempts were made to carry out reactions of this type on Ib. The concentrations of sulfuric acid-*d*₂ were varied from 100 to 10 mole %, and the temperature from 65 to 90°. In each case the n.m.r. spectrum shows that even after 20 hr. no detectable amount of deuteration had taken place.

The proton n.m.r. spectrum of 4-methyl-4,3-borazaroisoquinoline (Figure 1) consisted of a weak broad band centered at about τ 0.4, a sharp singlet at 1.75, a doublet at 1.85, a multiplet centered at 2.3, and a sharp singlet at 9.1, the integrated intensities being in the ratio 1:1:1:3:3. The broad peak at τ 0.4 clearly can be assigned to the NH proton, and the sharp peak at τ 9.1 to the methyl group. The singlet at τ 1.75 must correspond to the 1-proton which alone has no neighboring protons; the corresponding resonance also would be expected to occur at low field from analogy with isoquinoline. Three of the protons on the benzene ring account for the multiplet at τ 2.3, the fourth proton appearing at lower field (τ 1.85). The signal at τ 1.85 is a double doublet, corresponding to one strong (6.5 c.p.s.) and one weak (2 c.p.s.) coupling; these from analogy with other aromatic systems must correspond to couplings with an *ortho* and a *meta* proton, respectively. The signal at τ 1.85 therefore must correspond to a proton in the 5- or the 8-position.

A distinction between these two possibilities can be made with some certainty on the basis of MO calculations. Table I shows π -electron densities at the various positions in I, calculated by two variants⁶ of the Pople

(5) G. A. Olah, S. J. Kuhn, and S. H. Flood, *J. Am. Chem. Soc.*, **83**, 4571 (1961).

(6) A. L. H. Chung and M. J. S. Dewar, *J. Chem. Phys.*, **42**, 756 (1965); M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 685 (1965).

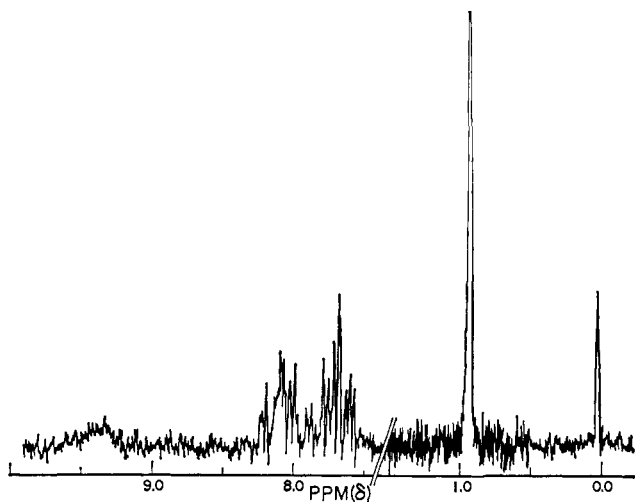


Figure 2. Proton n.m.r. spectrum of 8-bromo-4-methyl-4,3-borazaroisoquinoline in carbon tetrachloride.

SCF-MO method. The PPP values correspond to values for the repulsion integrals similar to those recommended by Pariser and Parr, while the SPO values correspond to a modified split p-orbital treatment. The calculations are taken from a forthcoming paper⁷ dealing with a number of heteroaromatic boron compounds; an independent check of the calculations has been provided by their success in interpreting the proton n.m.r. spectrum of 10,9-borazaronaphthalene.⁸

Table I. Calculated π -Electron Densities in 4-Methyl-4,3-borazaroisoquinoline

Position	SCF-MO PPP	SCF-MO SPO
1	0.747	0.746
2	1.334	1.339
3	1.729	1.683
4	0.296	0.361
5	0.961	0.946
6	0.978	0.990
7	0.983	0.975
8	0.987	0.997
9	1.020	1.015
10	0.963	0.954

Both the PPP and SPO methods agree in the prediction that the π -electron density in Ia should be much less in the 5-position than in the 8-position. The low-field signal therefore almost certainly corresponds to the 5-proton. Further support for this is provided by the proton n.m.r. spectrum of IIa (Figure 2); the low-field signal is still present in this, indicating that it does not correspond to the 8-proton. Both methods also predict similar π densities for the 6-, 7-, and 8-positions; this accounts for the fact that the corresponding signals occur together as a single complex multiplet.

The charge densities in Table I also lead correctly to the prediction that the 8-position in Ib should be the most reactive to electrophilic substitution. Charge densities are not in themselves a valid measure of

(7) M. J. S. Dewar and G. J. Gleicher, to be published.

(8) M. J. S. Dewar, G. J. Gleicher, and B. P. Robinson, *J. Am. Chem. Soc.*, **86**, 5698 (1964).

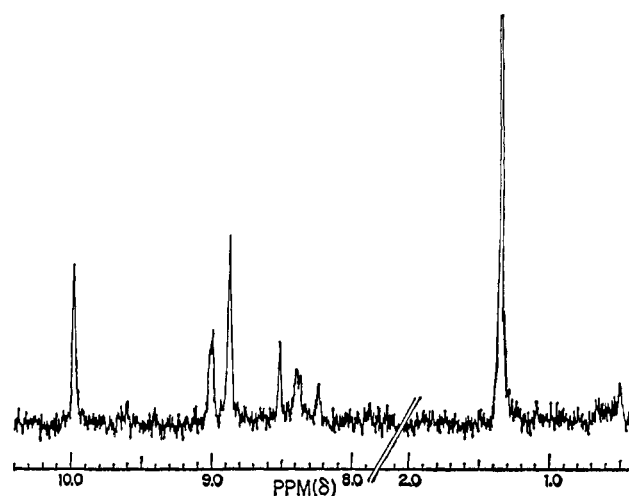


Figure 3. Proton n.m.r. spectrum of 8-nitro-4-methyl-4,3-borazaroisoquinoline in trifluoroacetic acid.

reactivity although a parallel between the two quantities often exists. It can be shown by a simple perturbation treatment⁹ that the charge density at a given position in a heteroaromatic system is not a measure of the absolute reactivity to substitution at that point, but rather of the case of substitution relative to that of the corresponding position in an isoconjugate hydrocarbon. Thus the charge densities in I should be measures of the reactivity relative to those in the corresponding positions in naphthalene. On this basis the SPO results once more agree well with experiment, in that they predict unambiguously that the 8-position should be much the most reactive to electrophilic substitution, for this is an α position, and the charge density there is greater than at any of the other positions in the benzenoid ring. Here again the PPP method seems inferior to the SPO; it would predict a much smaller difference in reactivity between the 5- and 8-positions.

Of course the charge densities listed in Table I are for the parent compound Ib, whereas nitration in sulfuric acid may well involve substitution in the conjugate acid. However protonation would not be expected to alter the orientation of substitution, although the conjugate acid should of course react much less readily. The resistance shown by Ib to deuteration, or to Friedel-Crafts acetylation, certainly indicates that salts of Ib are inert to electrophilic attack.

The proton n.m.r. spectrum of the mononitro derivative IIb was also interesting; since IIb was insoluble in nonplanar solvents, the spectrum was measured in trifluoroacetic acid solution (Figure 3).

The spectrum consists of a sharp singlet at τ 2.5, a doublet at 3.3, and a quadruplet at 4.1, with integrated intensities in the ratio 1:2:1. Clearly the low-field singlet corresponds to the 1-proton; this is shifted downfield in comparison with the corresponding signal for Ib, due to protonation of the 2-nitrogen of IIb in trifluoroacetic acid. The signal at τ 4.1 corresponds to a single proton split almost equally by two other protons (coupling constants 7 and 8 c.p.s.); the proton responsible for this signal must therefore be *ortho* to two other hydrogen atoms. The nitro group must therefore be in either the 5- or 8-position. The two

(9) M. J. S. Dewar, *Advan. Chem. Phys.*, **8**, 65 (1965).

remaining protons have almost identical chemical shifts, since their combined signal appears almost as a doublet.

Now the chemical shift of a proton *ortho* to a nitro group is greater than that of one *meta* or *para* to it, the two latter shifts being similar; thus the *ortho*, *meta*, and *para* protons in nitrobenzene show chemical shifts of τ -0.97 , -0.30 , and -0.42 , respectively.¹⁰ Now the protons corresponding to the τ 3.5 signal in IIB must lie, respectively, *ortho* and *para* to the nitro group; since their chemical shifts are the same in IIB, it follows that the chemical shifts of the corresponding protons in the parent compound Ib must have been different, the one *para* to the nitro group in IIB lying downfield in the n.m.r. spectrum of the parent compound Ib. This can be so only if the nitro group in IIB occupies the 8-position, as we have assumed, for the chemical shifts of the 6-, 7-, and 8-protons of Ib are very similar while the 5-proton signal appears downfield from the rest.

Experimental Section

4-Methyl-4,3-borazarisoquinoline was prepared by the method of Dewar and Dougherty.³

Bromination of 4-Methyl-4,3-borazarisoquinoline. A solution of bromine (0.02 mole) in acetic acid (18 ml.) was added dropwise with stirring to one of 4-methyl-4,3-borazarisoquinoline (0.02 mole) in acetic acid (100 ml.) at room temperature. After 7 hr., the deep orange crystals which formed were collected and warmed with a little distilled water, giving a pale yellow solid, m.p. 132–134°. Additional material was obtained by pouring the filtrate into water. Recrystallization from acetic acid and water gave 8-bromo-4-methyl-4,3-borazarisoquinoline (3.52 g., 84%) as white needles, m.p. 133–134°. *Anal.* Calcd. for $C_8H_8BBrN_2$: C, 43.05; H, 3.59; B, 4.93; Br, 35.87; N, 12.56; mol. wt., 222.9. Found: C, 43.18; H, 3.78; B, 5.06; Br, 35.75; N, 12.27; mol. wt., 223 (mass spectroscopy).

Degradation of the Bromination Product. Potassium permanganate (4 g.) was added to a suspension of the brominated material (1 g.) in boiling water (75 ml.) containing sodium carbonate (0.5 g.). The mixture was refluxed for 4 hr., cooled, acidified with sulfuric acid, and refluxed for an additional 45 min. The cooled solution was made basic with sodium hydroxide, filtered onto sulfuric acid and ice, and extracted with ether. The dried ($MgSO_4$)

ether extract was evaporated, giving *o*-bromobenzoic acid (0.30 g., 37%) which crystallized from benzene in white needles (m.p. 149–150°), not depressed by authentic *o*-bromobenzoic acid. *Anal.* Calcd. for $C_7H_5BrO_2$: C, 41.79; H, 2.49. Found: C, 41.91; H, 2.46.

Nitration of 4-Methyl-4,3-borazarisoquinoline. A solution of nitric acid (*d* 1.5, 0.002 mole) in sulfuric acid (10 ml.) was added dropwise with vigorous stirring to one of 4-methyl-4,3-borazarisoquinoline (0.02 mole) in sulfuric acid (50 ml.) at $0 \pm 2^\circ$. After 2.5 hr., the reaction mixture was poured onto water and ice. The resulting creamy solid (2.21 g.) crystallized from acetone and water in light tan needles (1.1 g.), m.p. 146–150° dec. Sublimation at 100° (1.0 mm.) gave pale yellow needles, m.p. 148–151° dec. *Anal.* Calcd. for $C_8H_8BN_3O_2$: C, 50.79; H, 4.23; B, 5.82; N, 22.2. Found: C, 50.99; H, 4.44; B, 5.86; N, 22.0.

Attempted Nitration of 4-Methyl-4,3-borazarisoquinoline with Nitronium Tetrafluoroborate. A solution of nitronium tetrafluoroborate (0.012 mole) in tetramethylene sulfone (25 ml.) was added with vigorous stirring to one of 4-methyl-4,3-borazarisoquinoline (0.014 mole) in tetramethylene sulfone at *ca.* 20°. After 1 hr., the reaction mixture was diluted with ether (100 ml.) and poured into water (800 ml.). Evaporation of the dried (Na_2SO_4) ether layer left unreacted 4-methyl-4,3-borazarisoquinoline which sublimed at 100° (0.25 mm.) in pale yellow crystals (1.4 g., 88%), m.p. 94–96.5°, not depressed by authentic 4-methyl-4,3-borazarisoquinoline.

Attempted Acetylation of 4-Methyl-4,3-borazarisoquinoline. A solution of 4-methyl-4,3-borazarisoquinoline (0.012 mole) in methylene chloride (35 ml.) was added slowly to an ice-cold suspension of aluminum chloride (0.024 mole) and acetyl chloride (0.012 mole) in methylene chloride (65 ml.). After 20 hr. at room temperature, the mixture was poured into cold, dilute hydrochloric acid, neutralized (Na_2CO_3), and extracted with ether, and the dried (Na_2SO_4) extracts were evaporated to give 4-methyl-4,3-borazarisoquinoline (1.60 g., 88.4%) which crystallized from ethanol-water in white needles, m.p. 97–98°, not depressed by authentic 4-methyl-4,3-borazarisoquinoline.

A similar experiment using stannic chloride instead of aluminum chloride gave 74% of unchanged 4-methyl-4,3-borazarisoquinoline.

Attempted Deuteration of 4-Methyl-4,3-borazarisoquinoline. A solution of 4-methyl-4,3-borazarisoquinoline in a mixture of sulfuric acid- d_2 (9.1 g.) and deuterium oxide (1.64 g.) was transferred to several n.m.r. sample tubes which were then heated to 68° in a thermostat. Tubes were removed at intervals for n.m.r. analysis; after 20 hr. no detectable deuterium exchange had occurred with any but the imine hydrogen.

Similar experiments using 100% sulfuric acid- d_2 at 65°, and deuteriosulfuric 10 mole % acid at 90°, were also unsuccessful.

Acknowledgment. We are grateful to the Robert A. Welch Foundation for financial support.

(10) P. L. Cario and B. P. Dailey, *J. Am. Chem. Soc.*, **78**, 3043 (1956).

Communications to the Editor

Stable Carbonium Ions. XIX.¹ Benzyl Cations

Sir:

We wish to report the direct observation of the benzyl cations I–VI and some preliminary observations concerning the effect of charge delocalization on the chemical shift of the positively charged benzylic hydrogens. The benzyl cations I–VI were prepared by careful addition of the corresponding benzyl chlorides to well-stirred SbF_5-SO_2 solutions at -75° .²

(1) Part XVIII: C. U. Pittman, Jr., and G. A. Olah, *J. Am. Chem. Soc.*, **87**, 5632 (1965).

(2) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *ibid.*, **86**, 1360 (1964).

