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-borazaroisoquinoline was prepared by the method of Dewar and Dougherty.[3]

Bromination of 4-Methyl-4,3-borazaroisoquinoline. A solution of bromine (0.02 mole) in acetic acid (18 ml.) was added dropwise with stirring to one of 4-methyl-4,3-borazaroisoquinoline (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-borazaroisoquinoline (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-borazaroisoquinoline. 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-borazaroisoquinoline (0.02 mole) in sulfuric acid (50 ml.) at 0 ± 2°. 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-borazaroisoquinoline 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-borazaroisoquinoline (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-borazaroisoquinoline 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-borazaroisoquinoline.

Attempted Acetylation of 4-Methyl-4,3-borazaroisoquinoline. A solution of 4-methyl-4,3-borazaroisoquinoline (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-borazaroisoquinoline (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-borazaroisoquinoline.

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

Attempted Deuteration of 4-Methyl-4,3-borazaroisoquinoline. A solution of 4-methyl-4,3-borazaroisoquinoline 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.

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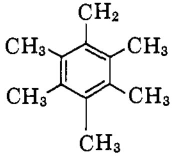
[10] P. L. Cario and B. P. Dailey, *J. Am. Chem. Soc.*, **78**, 3043 (1956).

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]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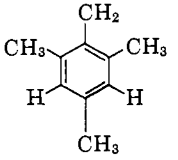
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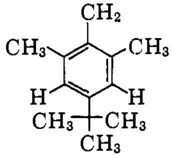
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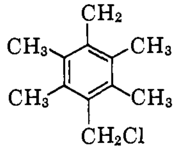
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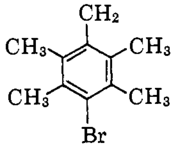
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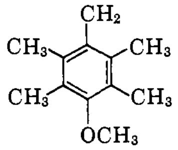
VI

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[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).

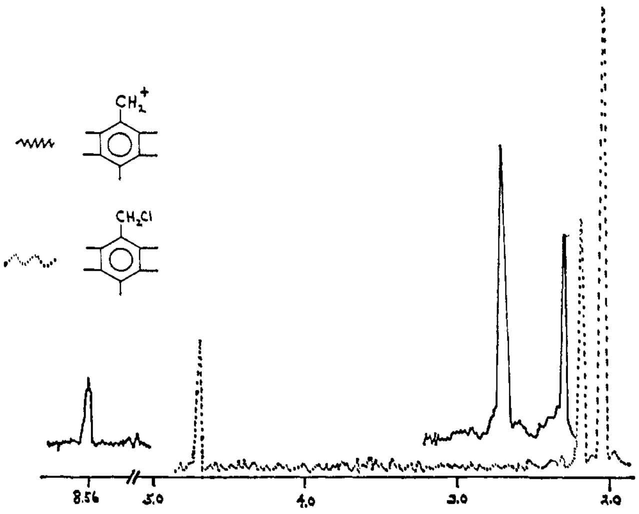


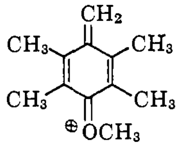
Figure 1.

In all cases the nmr spectra of these solutions at −65° exhibited well-resolved, substantially deshielded peaks which could be assigned from their position and their integrated areas. With the exception of ion II which slowly decomposes over a 0.5-hr period at −65°, all ions were stable indefinitely at this temperature.[3] A summary of the nmr band positions and assignments for ions I–VI is shown in Table I; an example of the simple spectra exhibited by all these ions is shown in Figure 1.

Table I. Nuclear Magnetic Proton Resonance Shifts of Benzyl Cations (in Parts per Million from External TMS at 60 Mc)

Compd	δ benzyl	chloride	δ carbonium ion	Δδ
I	α	4.70	8.66	3.96
	ortho	2.05	2.72	0.67
	meta	2.17	2.30	0.13
	para	2.05	2.72	0.67
II	α	4.58	8.50	3.92
	ortho	2.20	2.66	0.46
	meta	6.91	7.47	0.56
	para	2.07	2.66	0.59
III	α	4.67	8.67	4.00
	ortho	2.33	2.80	0.47
	meta	7.22	7.80	0.58
	para	1.20	1.33	0.13
IV	α	4.64	9.05	4.41
	ortho	2.17	2.78	0.61
	meta	2.17	2.38	0.21
	para	4.64	4.78	0.14
V	α	4.55	8.89	4.34
	ortho	2.22	2.73	0.51
	meta	2.22	2.54	0.32
VI	α	4.93	8.20	3.27
	ortho	2.29	2.95	0.66
	meta	2.37	2.65	0.28
	para	3.75	5.07	1.32

The positively charged benzylic hydrogens in ions I–VI exhibit large downfield shifts compared with the position of the benzylic hydrogens in the covalent benzyl chlorides (Figure 1). As charge delocalization in the carbonium ion increases, the benzylic hydrogens will be expected to be less deshielded. Thus, these hydrogens are least deshielded in ion VI (8.2 ppm), which suggests that resonance structure VII makes an important contribution to the stabilization of the ion.[4]



VII

The benzyl cations I and II have also been recently reported to exist in aluminum chloride–methylene chloride solutions.[5] However, the fact that under these conditions the most deshielded peak in the nmr spectrum of the 2,4,6-trimethylbenzyl cation (II) is due to the ring protons rather than the benzylic hydrogens strongly suggests that un-ionized species (possibly donor–acceptor complexes) were observed by these workers.

The chemical shift variations in ions I–VI (0.85 ppm) suggest the possibility of obtaining a correlation between charge densities and chemical shifts.[6] The limited examples which we have thus far studied are certainly in qualitative agreement with this idea. Further studies of *para*- and *meta*-substituted benzyl cations are necessary, however, before any attempt can be made at quantitative correlations.

We have also considered the possibility that the benzyl cations I–VI might undergo ring expansion to tropylium derivatives similar to the extremely facile rearrangement reported for the unsubstituted benzyl cation in the mass spectrum.[7] However, no evidence for skeletal rearrangement of ions I–VI was observed in solution.

Acknowledgment. The authors wish to express their gratitude to the National Science Foundation for support of this research and for a grant to Western Reserve University for the acquisition of nmr equipment.

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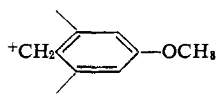
[3] The thermal stability of the pentamethylbenzyl cation (I) is remarkable. Substantial concentrations of this ion could still be detected after heating the ion in a sealed nmr tube at 75° for 15 min.

[4] The ability of a *para* substituent to stabilize a benzyl cation by resonance should be more pronounced when the substituent is coplanar with the benzene ring. In ion VI, the two methyl groups adjacent to the methoxyl group preclude the completely coplanar resonance structure VII. In an ion such as



the benzylic hydrogens should be much less deshielded.

[5] I. Hanazaki and S. Nagakura, *Tetrahedron*, **21**, 2441 (1965).

[6] T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963), and references therein cited.

[7] P. N. Rylander, S. Meyerson, and H. M. Grubb, *J. Am. Chem. Soc.*, **79**, 842 (1957); H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963; F. Meyer and G. Harrison, *J. Am. Chem. Soc.*, **86**, 4757 (1964).

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Stable Carbonium Ions. XX.[1] Phenyl- and Diphenylfluorocarbonium Ions

Sir:

We wish to record the preparation and direct observation of the first stable fluorocarbonium ions:

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[1] Part XIX: C. A. Cupas, M. B. Comisarow, and G. A. Olah, *J. Am. Chem. Soc.*, **88**, 361 (1966).