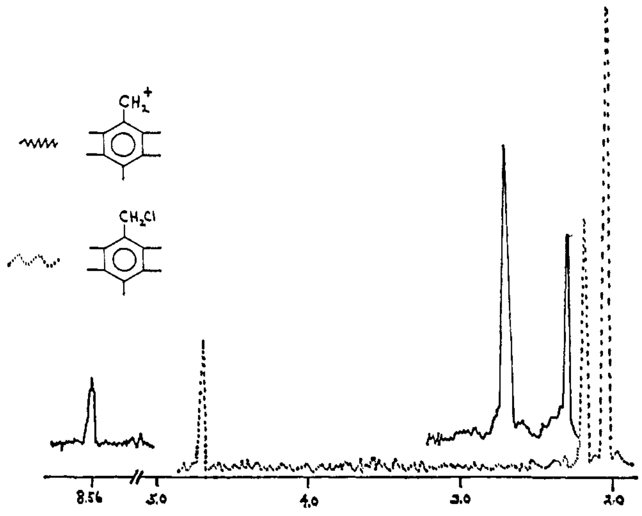


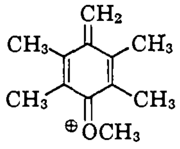
Figure 1.

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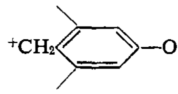
[3] The thermal stability of the pentamethylbenzyl cation (I) is remarkable. Substantial concentrations of this ion could still be detected after heating the ion in a sealed nmr tube at 75° for 15 min.

[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).

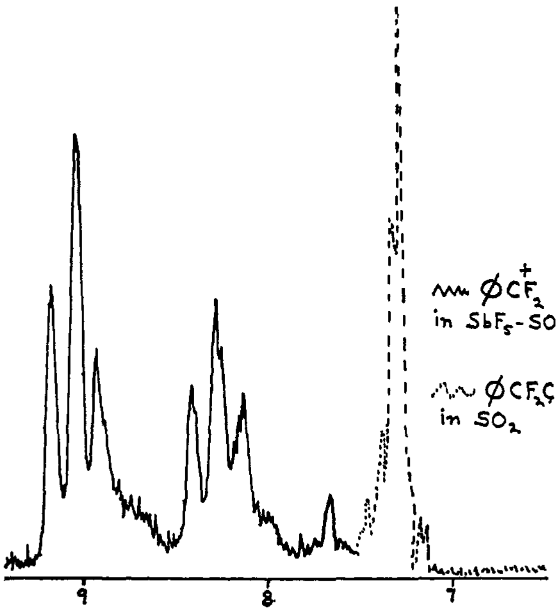


Figure 1.

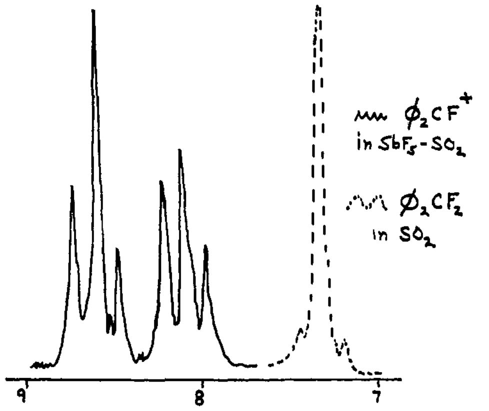


Figure 2.

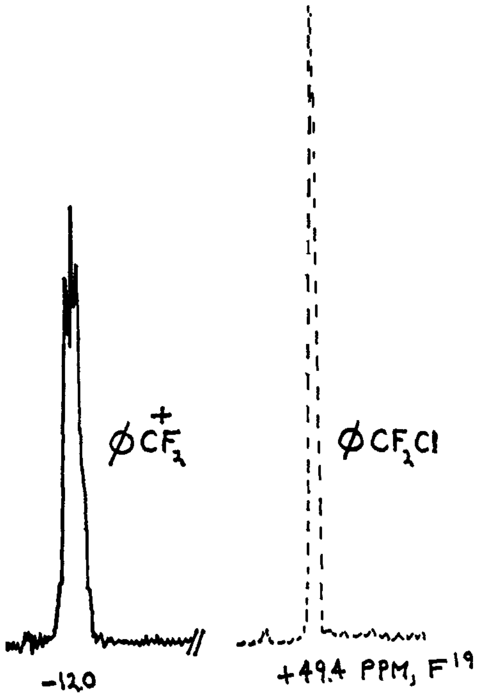


Figure 3.

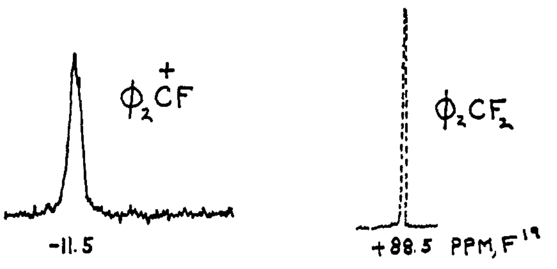
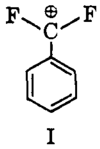


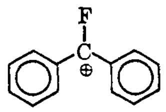
Figure 4.

the phenyl- and diphenylfluorocarbonium ions. We also report on the stabilizing effect of fluorine attached directly to a carbonium ion center and some further examples of long-range coupling through electron-deficient carbon atoms.

The fluorocarbonium ions I and II were prepared by

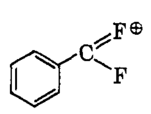


I

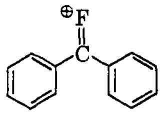


II

dissolving $C_6H_5F_2Cl$[2] (III) and $(C_6H_5)_2CF_2$ (IV)[3] in SbF_5–SO_2 solutions at −75°.[4] The pmr spectra (at −65°, ppm from external TMS) of I and II (Figures 1 and 2) showed extensive deshielding of the aromatic protons, indicating substantial charge delocalization into the benzene ring(s). As anticipated, the deshielding is more pronounced in the monophenyl ion I. That the stability of these ions results from substantial resonance contributions of type V and VI was confirmed most dramatically by examining the fluorine resonance of these ions.



V



VI

In I, the fluorine resonance (Figure 3) (in ppm from external CCl_3F at −60°) appears as a triplet (J_{HF} = 1 cps) deshielded 61 ppm from III (or 75.5 ppm from $C_6H_5CF_3$). Although other factors might contribute in deshielding the fluorine in ion I, the magnitude of this downfield shift suggests that a high degree of positive charge resides on the fluorine, as in the resonance structure V. The fluorine triplet in ion I is particularly interesting since similar long-range coupling across an sp^2 carbon atom has recently been observed for the dimethylethylcarbonium ion (*t*-amyl cation).[4]

The fluorine resonance of ion II (Figure 4) exhibits substantial deshielding, appearing 100 ppm downfield from IV. Long-range coupling of the fluorine with the four *ortho* protons is also discernible, although not resolved as in ion I. The fact that the line widths of the fluorine resonances of I and II are the same, however,

(2) Difluorochlorotoluene (III) was prepared by free-radical chlorination of α,α-difluorotoluene.[3] See also *Chem. Abstr.*, 31, 6675^6 (1937).

(3) W. R. Hasek, W. C. Smith, and V. A. Englehardt, *J. Am. Chem. Soc.*, 82, 543 (1960).

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

indicates that coupling is weaker in the latter ion. Charge density differences on the sp^2 carbon atom in ions I and II could be responsible for this behavior.

Despite the long-recognized ability of fluorine to form p-p(π) double bonds (as compared to chlorine and bromine), any manifestations of this behavior, especially in S$_N$1 type reactions, have been nullified by its inductive effect.[5] The stabilization accrued to carbonium ions with fluorine attached directly to the sp^2 carbon attests to its great resonance-electron-donating ability despite its high electronegativity.[6] Further studies of other carbonium ions with fluorine attached directly to the positive center are now in progress.

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.

(5) See J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 168, and references therein cited.

(6) In contrast to the stability of ion I in solution at −60°, benzyl cation undergoes rapid polymerization at this temperature.

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Formation of Cyclopropanes in Acid-Catalyzed Decomposition of Phenyldiazomethane in Olefins[1]

Sir:

Our interest in the mechanism of carbenoid cyclopropane formation[2] led us to examine the acid-catalyzed decomposition of phenyldiazomethane in olefinic solvents. Typical experiments involved the addition of trifluoroacetic acid to solutions of phenyldiazomethane in olefins at −70°.[3] Thermal decomposition of phenyldiazomethane was shown to be negligible under these conditions. Phenylcyclopropanes (I), benzylated olefins (II and III), and trifluoroacetates of structure IV constituted the main products besides 30–40% benzyl trifluoroacetate (V). Table I lists the product distribution obtained from reactions with olefins of various substitution patterns.[4] It should be noted that major fractions of cyclopropanes are formed only from olefins containing no tertiary carbon atoms. Furthermore, additions to *cis*- and *trans*-2-butene are completely stereospecific, leading to cyclopropanes in which the alkyl groups have the same geometrical relationship as in the olefins. The trifluoroacetates IV, however, are mixtures of *threo* and *erythro* isomers.[5]

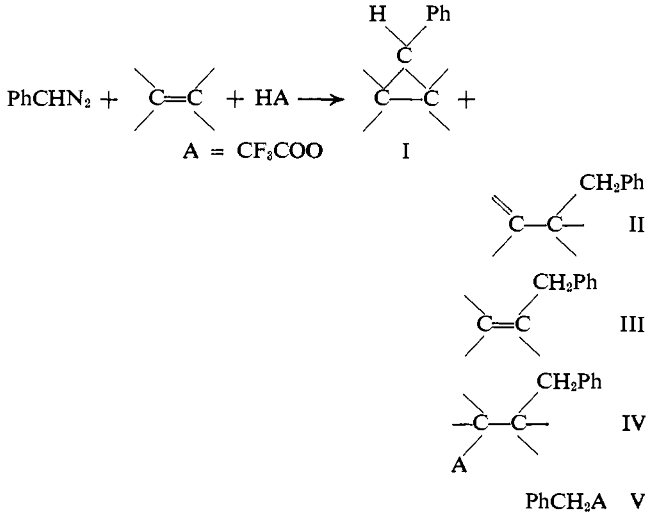

Table I. Product Distribution

Olefin	Product type (per cent of total I–IV) I	II	III	IV
2,3-Dimethyl-2-butene	1	98	. . .	1
Isobutene	2	64	20	14
trans-2-Butene	61	8^a	. . .	31^b
cis-2-Butene	51^c	21	6	22^b
1-Butene	38	32^a	. . .	30

^{a} This olefin may contain small amounts of III, due to imperfect glpc separation. ^{b} Mixtures of *threo* and *erythro* isomers. ^{c} Mixture of *syn* and *anti* isomers formed in a ratio of 1.2:1.

The use of excess deuteriotrifluoroacetic acid in the reaction with *trans*-2-butene led to incorporation of 21 atom % deuterium in I while II, IV, and V contained over 80%.[6] Similarly, when phenyldiazomethane-α-*d* was allowed to react with unlabeled acid, the deuterium content of I remained over 85%.

Mechanism studies on the acid-catalyzed decomposition of diphenyldiazomethane in polar solvents have established rate-limiting proton transfer as the first step.[7] The conjugate acid of the diazo compound, usually formulated as diphenylmethyldiazonium ion, is assumed to lose nitrogen in a fast step, yielding benzhydryl cation. An equivalent reaction scheme, however, cannot account for formation of I *and* the remaining products. If either benzyldiazonium ion or benzylcarbonium ion were precursors of the cyclopropane, the deuterium content of I as produced in the reaction with deuteriotrifluoroacetic acid should at least be one-half that of II and IV, and, most likely, should be significantly larger because of the expected isotope effect in the deprotonation step.[8] We therefore suggest that in the nonpolar medium of our experiments the diazo carbon functions as acceptor in hydrogen-bond formation with the acid, but that complete proton transfer is slow or comparable in rate with subsequent steps. Reaction of the olefin solvent with the hydrogen-bonded complex VI may lead either to I *via* the transition state VII or, through a less symmetrical transition state, to the ion pair VIII which then collapses to give

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(1) This work was supported by National Science Foundation Grant GP-4214.

(2) *Cf.* G. L. Closs and R. A. Moss, *J. Am. Chem. Soc.*, **86**, 4042 (1964); G. L. Closs and J. J. Coyle, *ibid.*, **87**, 4270 (1965).

(3) Although trifluoroacetic acid was studied in greater detail, other acids such as formic acid and anhydrous hydrochloric acid gave qualitatively similar results.

(4) The cyclopropanes were identified by direct comparison with previously prepared samples.[2] The trifluoroacetates IV were saponified, and the alcohols were compared with samples synthesized by standard methods. The structures of the olefins are fully supported by their infrared, nmr, and mass spectral data.

(5) The compositions of the isomer mixtures obtained from the two olefins are not identical. Configurations have not yet been assigned.

(6) The deuterium incorporation changes somewhat with the excess of acid employed, although the ratios of deuterium content of the various products remains practically constant. The trifluoroacetic acid was better than 95% deuterated as determined by nmr.

(7) D. Bethell and J. D. Callister, *J. Chem. Soc.*, 3801, 3808 (1963), and earlier references cited therein.

(8) A. A. Aboderin and R. L. Baird, *J. Am. Chem. Soc.*, **86**, 2300 (1964), estimate k_H/k_D for the loss of a proton from a bridged ion as ~3. The stereospecificity of the reaction requires that the ion produced from the addition of benzyl cation to the olefin would be bridged.