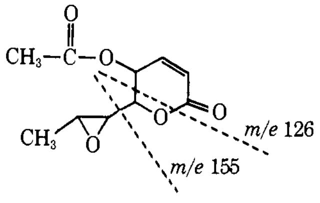
Isotope enrichment in asperlin was estimated to be 9% ± 1 per labeled carbon by comparison of signal intensities in the cmr spectrum. Enrichments determined by the proton–^{13}C satellite band areas are in Table I, which shows about 10 ± 0.5% per labeled carbon.

Table I. ^{13}C Enrichment Levels of Labeled Asperlin by ^{13}C–H Satellite Area

Carbon	$J_{^{13}C-H}$	Enrichment
C_8–H_3	126	11.5
C_{10}–H_3	130	10.9
C_4–H	152	10.0
C_2–H	174	10.8
C_6–H	165	*a*

[a] Complexity of satellite band prevented estimation of this value.

The mass spectrometric analysis demonstrated a difference in the ratios M + 1/M for the labeled and unlabeled asperlins of 0.366. This corresponds to an average of 7.3% ^{13}C enrichment at each of five positions, or a total of 8.4% ^{13}C (with natural abundance of 1.1% ^{13}C included) at each of the labeled carbons. Thus the approximate value of 8–10% ^{13}C deduced by nmr is confirmed and more accurately established by mass spectrometry.



asperlin, M = *m/e* 212

Qualitative distribution of the label could be observed by inspection of the isotope content of major fragments in the mass spectrum of labeled asperlin. For example, part of the label was located on the C_6, C_7, C_8 substituent, as indicated by the lower ^{13}C enrichment in fragments of mass 155 and 126. The label at the acetate could be observed directly in the CH_3CO peak (*m/e* 43), as well as indirectly by the loss of ketene from M, *m/e* 155, and *m/e* 126 to give *m/e* 170, 113, and 84, respectively, each with a reduced isotope enrichment. The latter two peaks nevertheless still contained some additional ^{13}C above natural abundance, demonstrating the presence of label also at carbons 1–4.

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Secondary Hydrogen–Deuterium Isotope Effects in the Fluorine Nuclear Magnetic Resonance Shifts of Methyl-*p*-fluorophenylcarbonium Ions[1,2]

Sir:

We have observed substantial secondary β-deuterium isotope effects on the fluorine nmr shifts of *p*-fluorophenylmethyl(H_3 and D_3)carbonium ions. These isotope effects are analogs of the well-known β-deuterium isotope effects on solvolysis rates,[3] although our measurements involve no state change, *i.e.*, are a physical property (presumably a ground-state charge distribution measure[4]) of the carbonium ion state. The effects of normal substituents on F nmr shifts of *p*-fluorophenyl derivatives have been found to show a remarkable correspondence to their effects on chemical reaction rates and equilibria.[5]

Measurable F nmr secondary β-deuterium isotope effects have been found (*cf.* Table I) only for *p*-fluorophenyl-labeled systems (ion or neutral) for which substantial stabilization by (methyl group) hyperconjugative interaction may be expected. Our results are consistent with those of Traficante and Maciel[6] for *m*- and *p*-fluorotoluene and their CD_3 derivatives, and, in the carbonium ions, the isotope effects are more than an order of magnitude larger than that found for the *p*-fluorotoluene system.

Although the secondary β-deuterium isotope effects on solvolysis rates have been generally interpreted in terms of hyperconjugative stabilization of the solvolysis transition state,[3,7] an interpretation in terms of nonbonded steric interactions has been advanced.[8,9] Steric isotope effects are undoubtedly involved in the rates of racemization of 9,10-dihydro-4,5-dimethylphenanthrene.[10]

In the present study of carbonium ions two lines of evidence (in addition to the single-state physical property nature of our measurement) have been obtained which indicate little or no steric interaction effects are involved in the observed β-deuterium F nmr shifts. (1) For the carbonium series I the β-deuterium isotope effect does not follow the steric size sequence X = H < OH, NH_2, < Me < CF_3, but instead follows the electronic sequence X = NH_2 < OH < Me < H < CF_3.[11] This latter order is expected for increased hyperconjugative demand from the carbinyl

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(1) This work was supported in part by the National Science Foundation. We are also grateful for support from NSF which made available to the UCI chemistry department the nmr spectrometer.

(2) Preliminary reports of this work were made at the Gordon Conference on Chemistry and Physics of Isotopes, Holderness, N. H., June 1968, and the Conference on Carbonium Ions, Cleveland, Ohio, Oct 1968.

(3) (a) E. S. Lewis and C. E. Boozer, *J. Amer. Chem. Soc.*, **74**, 6306 (1952); (b) V. J. Shiner, Jr., *ibid.*, **75**, 2925 (1953).

(4) R. W. Taft, F. Prosser, L. Goodman, and G. T. Davis, *J. Chem. Phys.*, **38**, 380 (1963).

(5) (a) R. W. Taft, *J. Amer. Chem. Soc.*, **79**, 1045 (1957); (b) R. W. Taft and L. D. McKeever, *ibid.*, **87**, 2489 (1965).

(6) D. D. Traficante and G. E. Maciel, *ibid.*, **87**, 4917 (1965).

(7) (a) V. J. Shiner, Jr., and C. J. Verbanic, *ibid.*, **79**, 373 (1957); (b) V. J. Shiner, Jr., *ibid.*, **82**, 2655 (1960); (c) V. J. Shiner, Jr., and G. S. Kriz, Jr., *ibid.*, **86**, 2643 (1964); (d) J. G. Jewett and R. P. Dunlap, *ibid.*, **90**, 810 (1968).

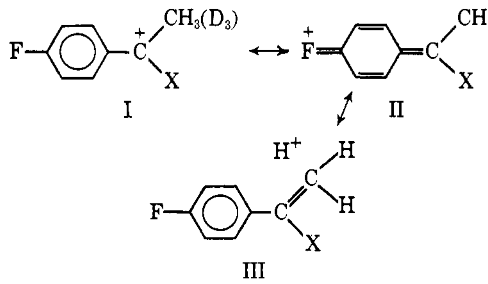
(8) L. S. Bartell, *ibid.*, **83**, 3567 (1961).

(9) (a) H. C. Brown and G. J. McDonald, *ibid.*, **88**, 2514 (1966); (b) H. C. Brown, M. E. Azzaro, J. G. Koelling, and G. J. McDonald, *ibid.*, **88**, 2520 (1966).

(10) K. Mislow, R. Graeve, A. J. Gordon, and G. H. Wahl, Jr., *ibid.*, **85**, 1199 (1963); **86**, 1733 (1964).

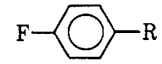
(11) *Cf.* R. W. Taft, R. H. Martin, and F. W. Lampe, *ibid.*, **87**, 2490 (1965).

center (valence bond forms II and III increase the direct exchange of positive charge between H and F with increased net electron withdrawal by the substituent



X). Indeed, there is an excellent correlation of the β-deuterium F nmr shifts for series I with the corresponding observed effects of substituent, X, on the F nmr shifts of the carbonium ions (Figure 1). (2) The removal of the CH_3 group from the steric environment of the *o*-phenyl hydrogen atoms by interposition of the spikelike -C≡C- linkage (*cf.* Table I) *does not* produce the major reduction in isotope effect expected if isotope effects in series I cations were predominantly the results of nonbonded repulsions between *o*-H's and CH_3 (or CD_3). Instead, the reduction to two-thirds of that found for the *p*-fluorophenyldimethylcarbonium ion is entirely reasonable for the fall-off through -C≡C- in the net electronic influence exerted by the greater vibrational amplitude of H than D. This conclusion is supported by the fact that the point for this cation also falls on the correlation line of Figure 1.

Table I. Fluorine Nuclear Magnetic Resonance Shielding and Isotope Effects for *p*-Fluorophenyl Derivatives



R	Solvent, °C	$\int_{\mathrm{ext}}{}^{a}$	$\int_{\mathrm{CD_3}}^{\mathrm{CH_3}}{}^{b,c}$
$C(CH_3)_2OH$	CCl_4, 25	+2.3	0.5 ± 0.5
	CH_3OH, 25	+6.5	0.0 ± 0.5
$C(CH_3)O$	CCl_4	−7.8	0.5 ± 0.5
	CH_3OH	−5.3	0.0 ± 0.5
$N(CH_3)_3{}^+I^-$	H_2O, 25	−2.6	−0.5 ± 0.5
	CH_3OH, 25	−0.9	0.0 ± 0.5
	HMPA, 25	−0.3	0.5 ± 0.5
$C(CH_3)NH_2{}^{+}$[d]	MA,[g] −40	−16.7	2.0 ± 0.5
$C(CH_3)OH^{+}$[e]	MA,[g] −40	−31.3	6.0 ± 1.0
$C{\equiv}C{-}C(CH_3)_2{}^{+}$[f]	MA,[g] −40	−36.5	8.0 ± 0.3[h]
$C(CH_3)_2{}^{+}$[f]	MA,[g] −40	−52.6	12.5 ± 0.5[h,i]
$C(CH_3)H^{+}$[f]	MA,[g] −40	−66.7	18.5 ± 0.5
$C(CH_3)CF_3{}^{+}$[f]	MA,[g] −40	−86.4	22.5 ± 0.5

[a] F nmr shifts in parts per million from tetrachlorotetrafluorocyclobutane (50% in $CHCl_3$ in external capillary); experimental error is ±0.1 ppm. [b] Isotope effects were measured in solutions containing both the heavy and light ions at concentrations less than 0.1 *M*. Positive signs denote resonance for CH_3 at higher field than CD_3. [c] Isotope effect for complete deuteration (unless otherwise specified) in hertz; divide by 56.4 to obtain parts per million. [d] Generated from the imine. [e] Generated from the ketone. [f] Generated from the carbinol. [g] Ions were generated by extraction from CH_2Cl_2 solutions into SbF_5–FSO_3H (1:4 by wt) solutions at −78° (G. A. Olah, M. B. Comisarow, C. A. Cupas, and C. U. Pittman, Jr., *J. Amer. Chem. Soc.*, **87**, 2997 (1965)). [h] Observed shift divided by statistical factor of 2. [i] Observed to be temperature independent for the interval −20 to −60°.

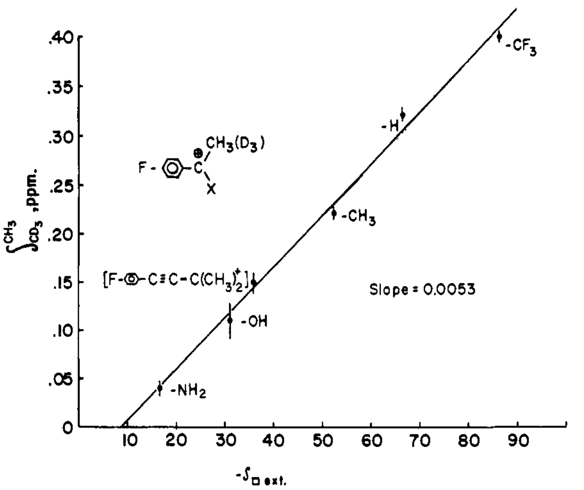
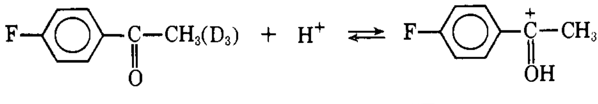
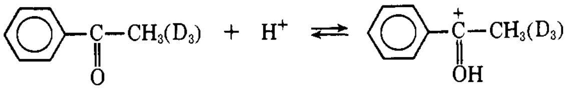


Figure 1. Secondary β-deuterium isotope effects on the F nmr shifts of X-substituted *p*-fluorophenylmethylcarbonium ions in magic acid, −40°: ordinate, $\int_{\mathrm{CD_3}}^{\mathrm{CH_3}}$, parts per million; abscissa, $-\int_{\mathrm{ext}}$, parts per million.

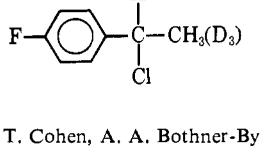
The 4′-methyl(H_3, D_3)-4-fluorobenzhydryl cation under similar conditions also gives a significant F nmr isotope effect of 3.5 ± 0.5 cps. The observation of this isotope effect represents still another system for which significant hyperconjugation is expected from a "noncrowded" methyl group.

Comparison of the β-deuterium F nmr and ΔG° isotope effects may be made for the following equilibria (eq 1 and 2).


(1)


(2)

For eq 2, Arnett, *et al.*,[12] observed $\int_{D} \Delta G^\circ$ = 0.15 kcal, a figure which may be expected to hold for eq 1 as well. Consequently, the coefficient between the F nmr shift accompanying eq 1 (0.11 ppm) and the corresponding standard free-energy charge is about 1 kcal/ppm. Coefficients of this magnitude for conventional substituent effects in systems of this kind have been previously reported.[5b] The coefficient of 1 kcal/ppm therefore appears useful in anticipating the corresponding equilibrium β-deuterium isotope effects on ΔG° for ionization to the other cations of Table I. Shiner and Pinnick[13] have measured the β-deuterium isotope effect for the solvolysis rate of *p*-$FC_6H_4C(CH_3,CD_3)_2Cl$ in 95% aqueous EtOH at 25° as k_H/k_D = 1.207 ± 0.003 (corrected to 100% D_6). Comparison with the F nmr shift for carbinol ionization (Table I) yields a coefficient of about 0.6 kcal in the free energy of activation per part per million shift on ionization in magic acid. The somewhat smaller coefficient is reasonable on grounds of incomplete ionization at the transition state. A still smaller extent of ionization in the solvolysis transition state of



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(12) E. M. Arnett, T. Cohen, A. A. Bothner-By, R. D. Bushick, and G. Sowinski, *Chem. Ind.* (*London*), 473 (1961).

(13) Private communication from V. J. Shiner, Jr., and H. R. Pinnick, Jr.

is indicated by the coefficient of about 0.4 kcal/mol in the free energy of activation[14] per part per million shift on ionization in magic acid.

Acknowledgment. We are pleased to acknowledge the assistance of Miss Karin Schneider in part of the experimental work. Helpful discussions with Dr. Stanton Ehrenson and Professors H. C. Brown, G. A. Olah, V. J. Shiner, Jr., and M. Wolfsberg are gratefully acknowledged.

[14] V. J. Shiner, Jr., W. E. Buddenbaum, B. L. Murr, and G. Lamaty, *J. Amer. Chem. Soc.*, 90, 418 (1968).

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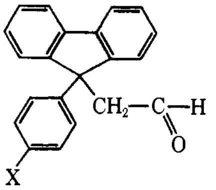
Substituent Effects at a Radical Migration Origin

Sir:

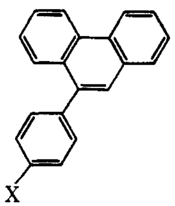
Free-radical aryl migrations have been under investigation by organic chemists for over two decades, but, except for the illuminating work of Rüchardt and coworkers[1] on the migratory aptitudes of substituted phenyl groups, little is known concerning the nature of the rearrangement transition state and the effects of substituents upon its stability. The interesting observation[2] that (9-phenyl-9-fluorenyl)acetaldehyde (**1**), upon peroxide-induced decarbonylation, gives a radical which undergoes 100% rearrangement with the exclusive migration of the phenylene ring prompted us to investigate the reaction further. Clearly, this system presents a unique opportunity to study the effects of various substituted phenyl groups at the migration origin of free-radical rearrangement reactions and avoids the possibility that such a group would compete in the rearrangement.

Accordingly, compounds, **1**, **2**, **3**, and **4** were synthesized for this purpose.



1, X = H
2, X = OCH$_3$
3, X = CH$_3$
4, X = Cl

These particular substituents were chosen because they correlated well in Rüchardt's work. All of the decarbonylation reactions were carried out under the same experimental conditions in the presence of benzyl mercaptan. In each case, 20 mol % of the mercaptan was added to a 0.5 *M* solution of the aldehyde in 1,2-dichlorobenzene. The solution was first degassed to remove oxygen and then it was maintained at 140 ± 0.01° and two quantities of di-*tert*-butyl peroxide consisting of 20 mol % each were added initially and after 120 min (40 mol % total amount), the total reaction time being 330 minutes. The rates of carbon monoxide evolution were measured and from these it was found that all four aldehydes undergo decarbonylation at the same rate, to the same extent, and presumably, therefore, by the same mechanism. The products, isolated by preparative tlc and column chromatography and characterized by elemental analysis and ir and nmr spectroscopy, were found to be 9-(*p*-X-phenyl)phenanthrenes **5**, 9,10-dihydro-9-(*p*-X-phenyl)phenanthrenes **6**, and 9-methyl-9-(*p*-X-phenyl)fluorenes **7** (X = OCH$_3$, CH$_3$, H, or Cl).



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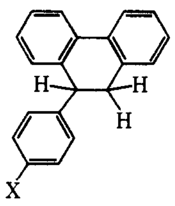

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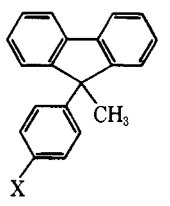


7

The product percentages were determined by nmr, and the results are shown in Table I.

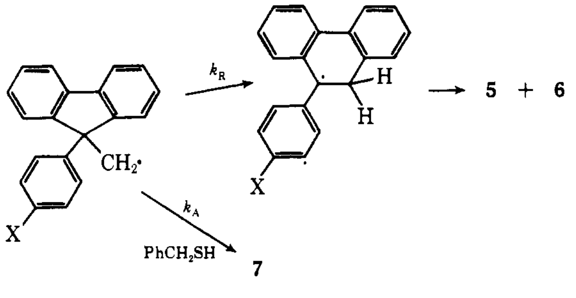
Table I. Product Percentages[a]

Substituent	% **5**	% **6**	% **7**
OCH$_3$	54	23	23
CH$_3$	54	26	20
H	53	28	19
Cl	54	31	15

[a] Error is ±1%.

When the reaction was run in the absence of the mercaptan no **7** could be isolated. The presence of the benzyl mercaptan thus has the effect of trapping the unrearranged radical to produce **7**. In the presence of mercaptan the initial radical formed by decarbonylation is involved in a competition between rearrangement and hydrogen atom abstraction as shown in Scheme I.

Scheme I



Assuming that the rate constant for hydrogen-atom abstraction, k_A, is independent of the substituent X (a reasonable assumption when one considers the distance of the substituent from the radical center), an equation can be developed which allows the calculation of the relative rate constants for the rearrangement steps.

$$\frac{\text{rearranged product}}{\text{unrearranged product}} = \frac{k_R}{k_A[\mathrm{PhCH_2SH}]} = \frac{\%\,\mathbf{5} + \%\,\mathbf{6}}{\%\,\mathbf{7}}$$

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[1] C. Rüchardt and R. Hecht, *Chem. Ber.*, 98, 2471 (1965), and preceding papers.

[2] B. M. Vittimberga, *Tetrahedron Lett.*, 2383 (1965).