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An Electron Spin Resonance Study of the Stereomutation in 1,1,3,3-Tetrafluoroallylic Radicals

Sir:

It is well known that simple allylic radicals are remarkably stable toward geometrical isomerization.[1] In a recent high-temperature esr study, we have shown that the allyl radical is static on the esr time scale even at 280° precluding a ΔG^* for internal rotation of less than 17 kcal/mol.[2] We wish to report now that the replacement of the terminal protons in the allyl radical by fluorines markedly increases the rate of internal rotation about the allylic bonds.[3] We find, furthermore, that halogen substituents in the 2 position (Ib, c) further decrease the activation energy to internal rotation (Cl > F). The latter effect is a manifestation of radical stabilization in β-haloalkyl radicals which is a topic of lively current interest.[4]

Ia, X = H
b, X = F
c, X = Cl

II
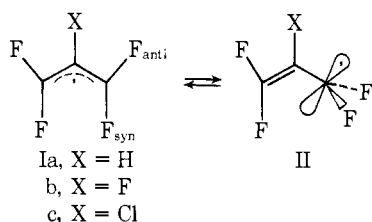
The 2-chlorotetrafluoroallyl radical Ic was generated photochemically in a cyclopropane–ethane solution from 2-chloro-3-bromotetrafluoropropene by reaction with tri(n-butyl)silyl radicals as bromine abstracting agents.[5] At −52° the esr spectrum consists of a quintet of 43.3 G without resolvable Cl hyperfine structure indicating four equivalent fluorines on the esr time scale. Lowering the temperature produces two types of line shape effects: first, a strongly viscosity-dependent broadening of all lines except the central peak and, second, an additional broadening of the $M_I = \pm 1$ and $M_I = 0$ lines. The first effect is related to the modulation of the large anisotropic component of the fluorine hyperfine A tensor by molecular tumbling (dipolar broadening)[6] while the second is caused by a slowing of the exchange of the terminal fluorines. The latter is complete at

−102° with the evolution of a triplet-of-triplets spectrum appropriate for two pairs of inequivalent fluorines. A fitting of the spectra by density-matrix line shapes calculations[7] based on noncorrelated exchange of the two pairs of syn and anti fluorines indicates a rate of 3×10^7 sec^{-1} at −80° and a ΔG^* of 4.5 kcal/mol for the exchange process.

The esr spectra of Ib (Figure 1) and Ia (Table I) can be obtained by the same method and are similarly temperature dependent. Fluxional spectral behavior, however, occurs at higher temperatures. A line shape analysis leads to Arrhenius plots from which activation free energies of 6.1 and 7.2 kcal/mol, respectively, can be extracted.

A mechanism for stereomutation based on a concerted exchange of the terminal fluorines brought about by disrotatory or conrotatory motion of the –CF₂ termini concomitantly with the closing of the $C_1C_2C_3$ angle cannot be excluded *a priori*. Calculated spectra for this mechanism do show a different evolution of the line shapes but the differences can easily be confused with the effects of dipolar broadening. The observation of the isomeric 2,2,3,3-tetrafluorocyclopropyl radicals from the corresponding bromides,[8] however, militates against such mechanism.

INDO calculations[9] for the coplanar perfluoroallyl (Table II) predict remarkably well the isotropic coupling constants for the terminal fluorines. The agreement is less satisfactory for F_2 although the *negative* sign for this coupling is in fact borne out by the experimental temperature dependence of its magnitude (Table I). Since the vibronic contribution to this coupling should become more positive as the temperature increases, owing to larger amplitudes for out-of-plane motions and hence increased possibilities for direct spin delocalization, the observed decreasing magnitude of $a(F_2)$ with increasing temperature clearly demands a negative sign for this coupling in the ground vibronic state. The calculations also predict a substantial unpaired spin density in the p_z orbitals on the terminal fluorines (19%) indicating an extension of the π allylic MO system over these fluorines. This result is consistent with the large anistropy of the A tensor inferred above from the pronounced dipolar line broadening effects.

The dramatic lowering of the rotational barriers in these radicals relative to the allyl radical itself is not entirely un-
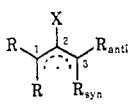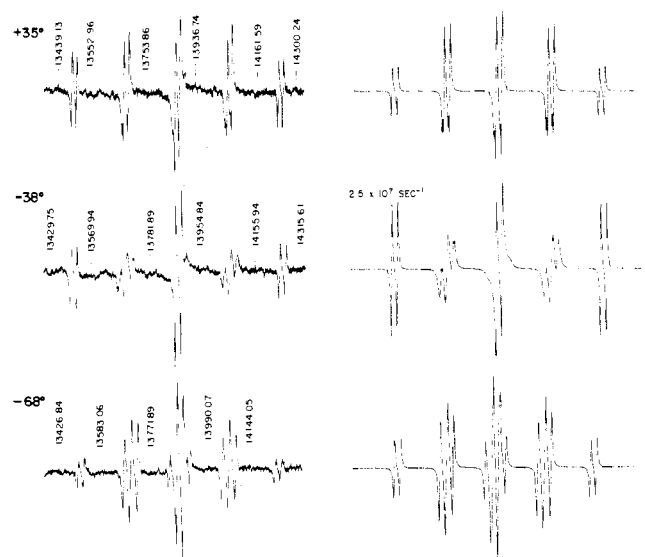

Figure 1. Esr spectra of the perfluoroallyl radical in cyclopropane. The calculated spectra (density matrix including higher order effects) refer to three conditions for the nonconcerted exchange of the terminal fluorines: fast exchange (top), $k = 2.5 \times 10^7$ sec^{-1} (middle), and slow exchange (bottom).

Table I. Esr Spectral Parameters of Fluoroallylic Radicals[a]

		Temp, °C	⟨g⟩	a(R_anti)	a(R_syn)	a(R)_ave	a(X)	ΔG*,[b] kcal/mol
R = H	X = H[c]	−130	2.00254[d]	14.81	13.90	14.36	4.06	>17[e]
R = H	X = H[e]	+230		14.82	14.00	14.41	4.53	
R = H	X = F	−60		14.86	13.88	14.37	9.18	
R_{1,1} = F, R_{3,3} = H	X = H[e]	−82	2.00325	F: 34.50 / H: 15.98	F: 29.29 / H: 15.21	F: 31.90 / H: 15.60	3.50	
R = F	X = H	−46	2.00424	42.56	39.72	41.14	3.33	7.2
		+26				41.62	3.60	
R = F	X = F	−95	2.00426	46.35	40.07	43.21	6.27	6.1
		−54		47.00	40.59	43.80	4.96	
		+40				43.97	3.97	
R = F	X = Cl	−102	2.00382	44.89	40.71	42.80	f	4.5
		−52				43.30	f	

"Magnitudes of the H and F isotropic hyperfine coupling constants (G)" spans the a(R_anti), a(R_syn), a(R)_ave, a(X) columns.

[a] The assignments of the larger coupling to the anti substituent on each terminal carbon atom are based on internal consistency with the 1-methallyl radicals (cf. ref 1c). [b] Activation free energy for the exchange of the terminal substituents. [c] Reference 1c. [d] R. H. Fessenden and R. W. Schuler, J. Chem. Phys., **39**, 2147 (1963). [e] Reference 2. [f] Unresolved.

Table II. Selected INDO Parameters for Allyl and Perfluoroallyl Radicals

		Unpaired pπ Spin densities				H and F isotropic hyperfine coupling constants (G)[c]	
Radical[a]	$\rho_z(C_{1,3})$	$\rho_z(C_2)$	$\bar{\rho}_z(F_{1,3})$[b]	$\rho_z(F_2)$	1,3[b]	2	
$CH_2{=}CH\dot{C}H_2$[d]	0.6240	−0.2479			−14.54 (−)14.36(exptl)	6.57 (+)4.06(exptl)	
$CF_2{=}CF\dot{C}F_2$[e]	0.5453	−0.2628	0.0482	−0.0207	39.40 (+)43.21(exptl)	−19.83 (−)6.27(exptl)[f]	

[a] Trigonal planar geometry energy optimized by varying the C–C distances. [b] Average values for syn and anti substituents. [c] Experimental signs consistent with the signs of the temperature coefficients (cf. text). [d] d(CH) = 1.08 Å, d(CC) = 1.38 Å. [e] d(CF) = 1.33 Å, d(CC) = 1.39 Å. [f] Unusually temperature-dependent increasing in magnitude with decreasing temperature (cf. text).

derstood as yet. Stabilization of the transition state II by the α-fluorine substituents seems unlikely since, on the basis of C–H bond dissociation energies, difluoromethyl and methyl radicals have comparable stabilities.[10] Steric repulsion between the syn fluorines in the planar structure I no doubt contributes to the destabilization of the ground state. We believe, however, that the effect is primarily of electronic origin and may be associated with a ground state destabilization due to electron–electron interaction. As indicated by the INDO calculations, the π MO's of Ib are delocalized over all atoms. By perturbation theory, the interaction of the pπ fluorine lone pairs with the singly occupied allyl π MO is weakly stabilizing while that with the doubly occupied π MO is destabilizing.[11] The magnitude of these conflicting effects should be inversely proportional to the energy separation between the interacting orbitals. The very low energy of the fluorine lone pairs[12] requires that the smaller energy separation and hence the larger interaction occurs between the lone pairs and the doubly occupied allyl π MO. This destabilizing interaction should therefore dominate, reducing the net allyl resonance energy and consequently lowering the rotational barrier.

The trend displayed by ΔG*_rot upon halogen substitution in the 2 position is best interpreted in terms of a stabilization of the perpendicular transition state II which is analogous to a β-chloroalkyl radical. These radicals are known to prefer the conformation in which the Cl atom is eclipsed by the half-filled p orbital, and a twofold barrier of about 4 kcal/mol has been estimated for $\dot{C}H_2CH_2Cl$.[4c] The CH_2CH_2F radical also has some proclivity to adopt the same conformation although in this case the latter represents only one of two stable rotamers.[4f] The details of this study, together with similar data for hydrocarbon allylic radicals substituted in the 2 position by heteroatoms, will be presented elsewhere.

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Communications to the Editor