of the exited singlet state, which would be an aromatic π,π^* state. Triplet sensitized excitation of a prenylarylsilane results in no 1,3-silyl migration: **1c** was intact when irradiated in the presence of benzophenone with longer wavelength light than 350 nm. In order to obtain kinetic profile for the photochemical 1,3-silyl migration, we have determined the fluorescence life time (τ_f) and the quantum yield (ϕ_f) for allyldimethylnaphthylsilane (**5**) and propyldimethylnaphthylsilane (**6**): τ_f values were 58.5 and 62.6 ns for **5** and **6**, respectively, and $\phi_f(5)/\phi_f(6)$ was 1.08. The rate and the quantum yield for the 1,3-silyl migration of **5** were thus estimated to be 1.03 × 10^6 s^{-1} and 0.06, respectively, where the rate constants for fluorescence, intersystem crossing, and the radiationless processes other than 1,3-silyl migration were assumed to be the same between **5** and **6**.
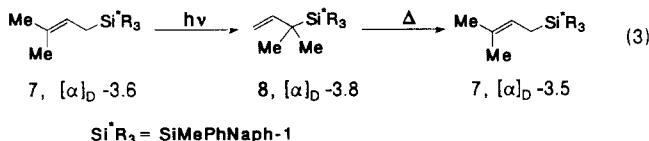
Irradiation of optically active prenylmethyl(1-naphthyl)phenylsilane (**7**, [α]$_D$ –3.6°, c 3.6, cyclohexane)[11] in hexane gave (2-methyl-3-buten-2-yl)silane **8**,[13] which showed [α]$_D$ –3.8° (c 3.2, cyclohexane) after purified with GPC. Although absolute configuration as well as optical purities of both the starting **7** and produced **8** were not determined, the stereochemical consequence of the photochemical migration was derived from the result of the further thermolysis of the isolated **8** ([α]$_D$ –3.8°) at 590 °C: The thermal isomerization of **8** gave **7** having [α]$_D$ –3.5°

(c 2.3, cyclohexane) after purification, whose value was essentially the same as that for the starting **7**, being indicative of the overall retention of configuration at silicon during the reaction sequence from **7** to **8** to **7** (eq 3).

$$Si^{*}R_3 = SiMePhNaph-1$$

Repeated runs gave similar results. Since the thermal 1,3-silyl migration has been confirmed to occur with complete inversion of configuration at the silicon atom,[3] the photochemical migration must also take place with inversion of configuration!

The results imply that the photochemical 1,3-silyl migration of allylsilanes follows suprafacial [1,3]-shift with inversion at silicon, in apparent disagreement with the prediction by the Woodward–Hoffmann rules:[14] During the migration the allylsilane molecule would jump from the funnel on the singlet excited surface to the ground-state surface at the similar molecular geometry to A in eq 1.

The isomer ratio between **1a** and **2a** at the photostationary state in pentane changed dramatically depending on temperatures. The ratio, **2a/1a**, changed from 2.06 to 6.22 between 0 and –90 °C. Excellent linear correlation between ln (**2a/1a**) and $1/T$ was observed with the correlation coefficient of 0.999$_6$. Further works should be required to reach the origin of this interesting temperature dependence.

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(11) Optically active **7** was prepared by the reaction of excess prenylmagnesium chloride with optical active chloro(1-naphthyl)phenylmethylsilane ([α]$_D$ –6.2°, cyclohexane; 98% ee)[12] in ether in 47% yield: ^{1}H NMR (CDCl$_3$) δ 0.59 (s, 3), 1.34 (s, 3), 1.54 (s, 3), 2.04 (d, 2, J = 8 Hz), 5.10 (t, 1, J = 8 Hz), 7.1–7.9 (m, 12).

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(13) **8**: ^{1}H NMR (CDCl$_3$) δ 0.70 (s, 3), 1.22 (s, 3), 1.23 (s, 3), 4.94 (d, 1, J = 17 Hz), 4.99 (d, 1, J = 11 Hz), 6.10 (dd, 1, J = 11, 17 Hz), 7.1–8.0 (m, 12). Isolation was achieved by a recycle GPC (Japan Analytical Industry Co., Ltd., an LC-08 Model with JAIGEL-1H and 2H column 20 mm ϕ × 600 mm).

(14) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

Reversal of the Nature of Substituent Effect by Changing the Number of the α-Substituent. Relative Ease of Formation of the Three α-Fluoromethyl Radicals

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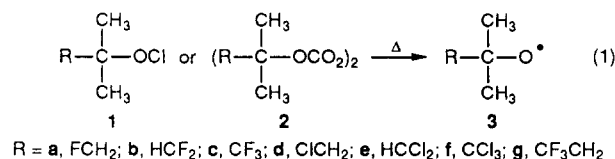
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Summary: The nature of α-F substituent effect on the methyl radical was found for the first time to change with the number of C–F bonds, i.e., it changes from the stabilizing effect in mono- and difluoromethyl radicals to the destabilizing effect in trifluoromethyl radical.

Sir: It is usually taken for granted that although the effect of successive substitution by a particular substituent Y on the same carbon atom is not necessarily additive, the nature of Y, e.g., whether electron-attracting or -donating, does not change in the YCH$_2$, HCY$_2$, CY$_3$ series.[1] Apparently, it has never been experimentally demonstrated that the nature of the substituent effect can be reversed in the aforesaid series. Some time ago, however, on the basis of the speculation that there could be two opposing aspects of the substituent effect of α-fluorine on the methyl radical, we proposed the following stability order, i.e., FCH$_2^{\bullet}$ and HCF$_2^{\bullet}$ > CH$_3^{\bullet}$ > CF$_3^{\bullet}$, in which the nature of

the α-F was inverted from spin-stabilizing to spin-destabilizing.[2] This paper presents conclusive epxerimental evidence that the nature of α-F substituent effect on the methyl radical indeed changes with the number of C–F bonds.

In a previous paper we have reported the relative rate of formation of CF$_3^{\bullet}$ and CH$_3^{\bullet}$ from the β-scission of a common precursor, the trifluoro *tert*-butoxy radical.[3] By using the same methodology, the relative rates of formation of FCH$_2^{\bullet}$, HCF$_2^{\bullet}$, and CF$_3$CH$_2^{\bullet}$ radicals, as well as ClCH$_2^{\bullet}$ and HCCl$_2^{\bullet}$, from the β-scission of alkoxy radicals **3**, have now been measured.

R = **a**, FCH$_2$; **b**, HCF$_2$; **c**, CF$_3$; **d**, ClCH$_2$; **e**, HCCl$_2$; **f**, CCl$_3$; **g**, CF$_3$CH$_2$

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(1) (a) Merenyi, R.; Janouseck, Z.; Viehe, H. G. In *Substituent Effects in Free Radical Chemistry*; Viehe, H. G., et al., Eds.; Reidel Publishing Co.: Dordrecht, The Netherlands, 1986; p 301. (b) Susmann, R. *Ibid.* p 143. (c) Birkhofer, H.; Beckhaus, H. D.; Ruechardt, C. *Ibid.* p 199.

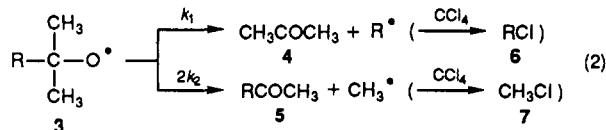(2) Fluorocarbon Group of SIOC, *Sci. Sin. (Engl. Ed.)* **1977**, *20*, 353.
(3) Jiang, X. K.; Li, X. Y.; Wang, K. Y. *J. Chem. Soc., Chem. Commun.* **1986**, 745.

Table I. Percentage Yields of Thermolysis Products of the Hypochlorites 1a and 1b and the Peroxy Dicarbonates 2a and 2b in CCl$_4$

precursor	products	% yield[b]	
		1, 160 °C	2, 140 °C
1a, 2a	FCH$_2$COCH$_3$	11.8 ± 1.0	9.1 ± 1.0
	FCHClCOCH$_3$	1.4 ± 1.0	—[d]
	CH$_3$COCH$_3$	41.0 ± 2.0	42.3 ± 2.0
	ClCH$_2$COCH$_3$	14.9 ± 1.0	<1.0
	HCCl$_2$COCH$_3$	0.5 ± 0.5	—[d]
	CH$_3$Cl	11.4 ± 1.0[c]	5.8 ± 1.0[c]
	FCH$_2$Cl	52.9 ± 2.0[c]	44.2 ± 2.0[c]
1b, 2b	HCF$_2$COCH$_3$	15.7 ± 1.0	10.0 ± 1.0
	CH$_3$COCH$_3$	68.5 ± 4.0	49.2 ± 2.0
	ClCH$_2$COCH$_3$	5.2 ± 1.0	<2.0
	HCCl$_2$COCH$_3$	<0.5	—[d]
	CH$_3$Cl	13.0 ± 1.0[c]	6.8 ± 1.0[c]
	HCF$_2$Cl	61.1 ± 4.0[c]	40.4 ± 2.0[c]

[a] All products were identified with authentic samples by means of GC and ^{1}H and ^{19}F NMR analyses and confirmed by GC–MS analyses. [b] Measured by GC calibrated with authentic samples and confirmed by ^{1}H, ^{19}F NMR spectroscopy. [c] Estimated by ^{1}H and ^{19}F NMR spectroscopy only. [d] Not detectable.

Table II. Percentage Yields of Thermolysis Products of the Hypochlorites 1e and 1g in CCl$_4$ (160 °C) and the Peroxy Dicarbonate 2d in BrCCl$_3$ (140 °C)

precursor	products	% yield[b]
2d	ClCH$_2$COCH$_3$	3.6 ± 0.4
	CH$_3$COCH$_3$	41.8 ± 2.0
	BrCH$_2$COCH$_3$	0.9 ± 0.4
	CH$_3$Br	3.2 ± 0.4[c]
	BrCH$_2$Cl	35.9 ± 2.0
1e	HCCl$_2$COCH$_3$	2.7 ± 0.2
	CH$_3$COCH$_3$	66.7 ± 3.0
	ClCH$_2$COCH$_3$	10.2 ± 0.5
	CH$_3$Cl	2.3 ± 0.5[c]
	HCCl$_2$	71.7 ± 3.0
1g	CF$_3$CH$_2$COCH$_3$	53.3 ± 2.0
	CF$_3$CH$_2$COCH$_2$Cl	1.8 ± 0.5
	CH$_3$COCH$_3$	6.2 ± 0.5
	ClCH$_2$COCH$_3$	7.7 ± 0.5
	HCCl$_2$COCH$_3$	0.5
	CH$_3$Cl	43.3 ± 2.0[c]
	CF$_3$CH$_2$Cl	9.3 ± 1.0

[a] All products were identified with authentic samples by means of GC and ^{1}H and ^{19}F NMR analyses and confirmed by GC–MS analyses. [b] Measured by GC calibrated with authentic samples and confirmed by ^{1}H, ^{19}F NMR spectroscopy. [c] Estimated by ^{1}H and ^{19}F NMR spectroscopy only.

The hypochlorites 1 and percarbonates 2, synthesized by known methods or our modified procedures,[4] were thermolyzed in CCl$_4$ to produce the alkoxyradicals 3a–g, which underwent β-scission and yielded the radicals CH$_3$· and R·.

$$R-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O \cdot \quad \overset{k_1}{\underset{2k_2}{\rightleftharpoons}} \quad \begin{array}{l} CH_3COCH_3 + R \cdot \ (\xrightarrow{CCl_4} RCl) \\ \mathbf{4} \qquad\qquad\qquad\qquad \mathbf{6} \\ RCOCH_3 + CH_3 \cdot \ (\xrightarrow{CCl_4} CH_3Cl) \\ \mathbf{5} \qquad\qquad\qquad\qquad \mathbf{7} \end{array} \quad (2)$$

Carbon tetrachloride served both as the solvent and the radical scavenger.[5] As reported previously,[3] all products from β-scission and other side reactions were identified and quantified by comparison with authentic samples using GC, GC–MS, ^{1}H and ^{19}F NMR, and products derived from radical combination processes were not detected. Besides the primary products, i.e., acetone 4 and the ketones 5, there are secondary products derived from the chlorination of 4 and 5. Thus the rates of formation of R· relative to CH$_3$· should be:

$$k_{rel} = \frac{k_1}{k_2} = \frac{[4] + [\text{chlorinated } 4]}{0.5\{[5] + [\text{chlorinated } 5]\}} = \frac{[6]}{[7]} \quad (3)$$

The quantitative yields of the products relevant to the calculation of the k_{rel} in the thermolysis of 1a,b,e,g and 2a,b,d are listed in Tables I and II. The k_{rel} values are calculated from the yields of 4 and 5 and their chlorinated derivatives,[6] and the k_{rel} values for CF$_3$· and CCl$_3$· are taken from previous work.[3] With the rate of formation of CH$_3$· as the standard (k_{rel} = 1), we can now present the order of increasing k_{rel} values for the variously substituted methyl radicals as shown in Table III. The k_{rel} values from the thermolysis of 2 are in good agreement with those from the hypochlorite 1 experiments.

The effect of fluorine substitution on the stability of radicals has been extensively investigated, both theoreti-

cally[7] and experimentally.[8] However, the results reported are contradictory. In a most recent review,[1] on the basis of various data, fluorine is considered to be a destabilizing group (Viehe's RRS$_X$ = −1.4), but the value evaluated in this lab is approximately zero,[9] i.e., its effect on α-spin is small. In fact, in most all of the important approaches to the evaluation of σ·, the fluorine is placed on the para position of a benzyl radical, thus the effect of fluorine substitution is very likely attenuated and may not be accurately measurable. This fact, therefore, argues in favor of our β-scission approach.

Our data reveal that the methyl radical is stabilized by one α-fluorine, but the stabilizing effect of the second fluorine is barely noticeable. Of particular interest, however, is the observation that the third fluorine can actually reverse the nature of the substituent effect of α-fluorine, i.e., the stabilizing effect, is changed into a destabilizing effect.

If the relative stabilities of the products, i.e., acetone and halogenated acetones RCOCH$_3$ 5, are taken into consideration, the polar effect might favor the formation of acetone.[8a,11a] In other words, without the polar effect the CF$_3$ cleavage of 1c or 2c would be even slower. Furthermore, the polar effects on the FCH$_2$ and HCF$_2$ cleavages would be definitely smaller than that on CF$_3$ cleavage. Thus, in the absence of the aforesaid "ketone stability" effect, the differences between the k_{rel} value of CF$_3$· and those of HCF$_2$· and FCH$_2$· radicals could even be larger than those actually observed.

(4) (a) Wang, K. Y. Ph.D. Thesis, Shanghai Institute of Organic Chemistry, 1988. (b) Preparation of hypochlorites 1 and percarbonates 2 as well as other experimental data will be published in a full paper.

(5) For the thermolysis of peroxy dicarbonate 2d (i.e., R = ClCH$_2$), BrCCl$_3$ was used instead of CCl$_4$ to avoid the chlorination of acetone, which would interfere with the quantitative treatment of the product analysis.

(6) In principle, the [6]/[7] ratio should yield the same k_{rel} (eq 3), but experimentally this value was found to be less precise or certain (see footnote c in Table I), because of their volatility.

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(8) (a) Walling, C.; Padwa, A. J. Am. Chem. Soc. 1963, 85, 1593. (b) Shelton, J. R.; Liang, C. K. J. Org. Chem. 1973, 38, 2301. (c) Creary, X. J. Org. Chem. 1986, 51, 1110. (d) Dolbier, W. R., Jr.; Piedrahita, C. A.; Al-Sader, B. H. Tetrahedron Lett. 1979, 2957. (e) Smart, B. E. In Supplement D: The chemistry of halides, pseudohalides and azides; Patai, S., Ed.; Wiley: London, 1983; p 620. (f) Dust, J. M.; Arnold, D. R. J. Am. Chem. Soc. 1983, 105, 1221.

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Table III

| R	CF$_3$•	CF$_3$CH$_2$•	CH$_3$•	FCH$_2$•	HCF$_2$•	ClCH$_2$•	HCCl$_2$•	CCl$_3$•
k_{rel} (1, 160 °C)	0.09	0.52	1.0	8.6	9.5	–	59	62
k_{rel} (2, 140 °C)	0.08	–	1.0	9.0	10.2	22	–	–

Recently, there have been quite a number of examples which show that two substituents directly bonded to the radical center usually do not lead to an additive effect on the stability of the radical. Some authors have suggested that it can be either synergistic or antagonistic, depending on whether the two substituents are of opposite or similar polarity.[10] To our knowledge, however, there is no previous report which demonstrates that the nature of the substituent effect can be completely reversed by increasing the number of the same substituent.

Although many reports imply that monochlorine substitution stabilizes a radical,[8] there appears to be no direct experimental data on di- and trichloromethyl radicals. Our results show that the stabilizing effect of α-chlorine substitution progressively increases with the number of the chlorine substituent. However, it is noteworthy that the second chlorine makes its presence strongly felt, but the effect of the third chlorine is rather small.

The α-CF$_3$ substituent appears to exert a slightly destabilizing effect on the methyl radical. The small difference of k_{rel} values between CF$_3$CH$_2$• and CH$_3$• could also be a reflection of a very week ground-state polar effect on the strengths of the R–CMe$_2$O• bonds.[11] The σ• values and other data suggest that the effect of the α-CF$_3$ group is either negligible or slightly destabilizing.[8,9]

It is interesting to note that Pasto's most recent theoretical calculations[12] predict the following order of relative stabilities:

$$CF_3• < CF_3CH_2• < CH_3• < HCF_2• < FCH_2• < ClCH_2• < HCCl_2• < CCl_3•$$
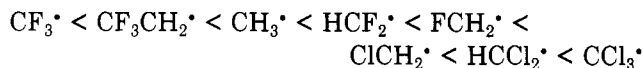
It is qualitatively in good agreement with our experimental results.

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A Reliable Method for Fast Atom Bombardment Mass Spectrometric Analysis of α-Aryl 1,2-Diols. Formation of Lithium–Diol Adducts

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Summary: An operationally simple and reliable method for obtaining molecular ion information on α-aryl 1,2-diols using fast atom bombardment mass spectrometry is described. Analysis entails formation of lithium–diol adducts using a solution of LiCl and matrix solvent and then bombarding the sample with either xenon atoms or cesium ions to afford [MLi]$^+$ ions.

Sir: The analysis of 1,2-diols by electron impact mass spectrometry (EIMS) has always been troublesome.[1] In general, these compounds give rise to little or no molecular ion using this technique. A general remedy for this problem has been chemical derivatization of the bifunctional group. However, this necessitates an additional synthetic step as well as ensuring that nothing happens to the product upon derivatization (e.g. decomposition, rearrangement, etc.). Many elegant studies concerning stereochemical effects in the chemical ionization mass spectra (CIMS) of diols have been reported.[2] One drawback of this technique is that like EIMS, the compounds being analyzed must be sufficiently volatile to allow for vaporization in vacuo. Fast atom bombardment mass spectrometry (FABMS) is commonly used to obtain molecular ion and structural information on polar molecules and therefore seemed perfectly suited for the analysis of a range of vicinal diols. However, during the course of a project involving the development of an efficient method for coupling two different carbonyls (pinacol cross coupling)[3] we found that FABMS analysis of α-aryl 1,2-diols does not always provide molecular ion information. Herein we present a practical method for the analysis of such diols via FABMS which involves formation of a lithium–diol complex.

The detection of protonated molecular ions ([MH]$^+$) in the FABMS of 1,2-diaryl-1,2-ethanediols (1), 1-aryl-2-alkyl-1,2-ethanediols (2), and 1-aryl-1,2-dialkyl-1,2-ethanediols (3) was only moderately succesful employing a range of matrices. In general, compounds 1 and 3 gave no molecular ion information whereas compounds 2 produced variable results. The major difficulty in the analysis of compounds 1, 2, and 3 is the instability of the protonated molecular ion with respect to loss of water (i.e. [MH – H$_2$O]$^+$ is always observed).[4] We felt that replacing the

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