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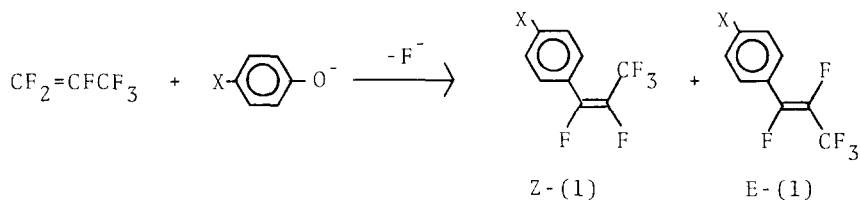
SHORT COMMUNICATION

Electronic Effect of Aryl Groups on the Z/E Ratio of  
1-Aryloxy-pentafluoropropenes

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It is well known that hexafluoropropene and O-nucleophiles easily give addition and substitution products, depending on reaction conditions and on the type of nucleophile [1-3]. In a previous paper [3], we have reported that the nucleophilic reaction of hexafluoropropene with sodium aryloxide in tetrahydrofuran gives a mixture of Z and E isomers of 1-aryloxy-pentafluoropropene, and that the Z/E ratio seems to depend on the nature of the aryl group. Further study on this problem has been made, and it was found that the Z/E ratio is correlated with the electronic properties of the substituents X.



The mixture obtained from the reaction between hexafluoropropene and a sodium p-substituted aryloxide in tetrahydrofuran at 5 °C was subjected to <sup>19</sup>F nmr analysis, and the Z/E ratios of the substitution products were determined. The

TABLE 1  
 $^{19}\text{F}$  NMR Data for 1-Aryloxy-1,2,3,3,3-pentafluoropropenes

Z-(1)

E-(1)

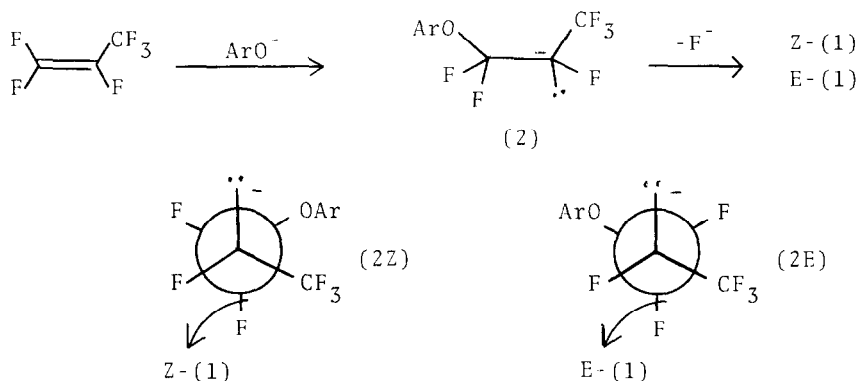
X	Chemical Shifts ( $\delta$ ppm) <sup>a</sup>							Z/F <sup>b</sup>	$\sigma_p(X)^c$
	Z		E						
	F <sup>a</sup>	F <sup>b</sup>	F <sup>a</sup>	F <sup>b</sup>	F <sup>c</sup>	F <sup>c</sup>	F <sup>c</sup>		
CH <sub>3</sub> O	-9.5	103.8	13.8	-9.5	110.8	29.6	26/74	-0.268	
CH <sub>3</sub>	-10.0	102.5	13.1	-10.0	109.6	29.0	35/65	-0.170	
H	-9.8	102.1	13.2	-9.8	108.7	29.0	41/59	0	
Cl	-10.0	101.4	14.2	-10.0	108.4	30.1	42/58	+0.227	
Br	-10.2	100.1	13.5	-10.2	106.5	29.2	42/58	+0.232	
NO <sub>2</sub>	-9.2	99.6	15.2	-9.2	106.0	30.6	46/54	+0.778	

a) The values are given upfield from ext. CF<sub>3</sub>CO<sub>2</sub>H. b) The ratios were based on the signal intensities of their  $^{19}\text{F}$  nmr. c) L. P. Hammett, "Physical Organic Chemistry", McGraw-Hill (1970), p. 356.

results are shown in Table 1. The Z/E ratio is evidently correlated with the electronegativity of the substituent, and the more electronegative X is, the more Z-isomer, or the less E-isomer, is formed.

As the reaction was carried out at low temperature ( $5^{\circ}\text{C}$ ), the formation of the isomers must be controlled kinetically, in other words, must be influenced by the conformational stability of the reactive intermediate.

In these kinds of nucleophilic reactions, it is proposed that they generally proceed through the  $\text{E1cB}$ -like mechanism via carbanion (2) [2]. From the conformation of carbanion (2Z), as shown below, trans elimination of fluoride ion should give the Z-(1) isomer, whereas from the conformation of (2E), it should give E-(1) isomer.



Inspection of the structures reveals that the conformation (2E) is energetically more preferable to (2Z), because on consideration of the steric and electronic repulsions between the trifluoromethyl and aryloxy groups, the former is less hindered than the latter. This effect would generally cause the predominant formation of the E-(1) isomer, as was actually observed.

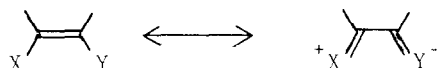
When an electron-withdrawing substituent is introduced into the benzene ring, the density of unshared electron pairs on the oxygen atom of the ether-linkage will decrease, weakening the repulsion between electron pairs of the oxygen and fluorines of the trifluoromethyl group. This effect will

result in increase in formation of the Z-isomer, because carbanion (2Z) will be less destabilized.

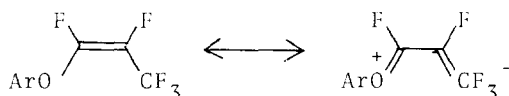
Electron donative substituents, on the other hand, will increase the electron density of the oxygen atom, making formation of the Z-isomer more difficult. Thus, p-methoxyphenoxide ion affords much more E-isomer than p-nitrophenoxide ion. From the above observations, it is apparent that the Z/E ratio is correlated with the substituent's constant of Hammett's equation, though it is not directly proportional (Table 1).

Naturally, the kinetically controlled Z/E ratios discussed above should be different from those controlled thermodynamically, i.e., the Z/E ratios in equilibrium states. In order to ascertain this, a kinetically controlled mixture of 1-(p-methoxyphenoxy)pentafluoropropene containing Z and E isomers in the ratio of 26/74 was heated with fluoride ion in solvents, such as sulfolane or dimethylformamide. The resulting mixture was found to contain Z and E isomers in the ratio of 55/45, which reveals that the Z form is slightly more stable than the E-form thermodynamically.

For a series of 1,2-disubstituted olefins where the substituents contain unshared electron pairs, it is generally observed that the cis form is more stable than trans form. This is suggested to result from resonance contribution by ionic forms, where the interaction between the positive and negative dipoles is energetically more favorable in the cis rather than the trans form [4].



Taking into account resonance involving negative hyperconjugation of the trifluoromethyl group, the following interaction between dipoles for Z-(1) must contribute to the thermodynamical stability.



## EXPERIMENTAL

Determination of the Z/E ratios

A mixture of sodium aryloxide (0.025 mol) and dried tetrahydrofuran (30 ml) was placed in a pressure vessel made of glass and cooled to  $-60^{\circ}\text{C}$  in a dry ice-acetone bath. After introduction of hexafluoropropene (3.60 g, 0.025 mol) into the vessel, the whole was brought to  $5^{\circ}\text{C}$  in an ice bath, and was stirred for 4 h at that temperature. The reaction mixture was filtered to remove insoluble materials, such as unreacted sodium aryloxide and formed sodium fluoride. Part of the filtrate was taken in a sample tube and subjected to  $^{19}\text{F}$  nmr analysis. The analysis was performed at  $35^{\circ}\text{C}$  using the Hitachi Nucleomagnetic Resonance Spectrometer Type R-24F. The chemical shifts of each isomer are shown in Table 1, being expressed in ppm from external trifluoroacetic acid. The Z/E ratios of the products were determined from the signal intensities of each isomer.

Determination of the Z/E ratio of 1-(p-methoxyphenoxy)pentafluoropropene in equilibrium

A mixture of 1-(p-methoxyphenoxy)pentafluoropropene with Z/E ratio of 26/74 (2.54 g, 0.01 mol), potassium fluoride (0.06 g, 0.001 mol) and sulfolane (25 ml) was stirred for 7 h at  $85-90^{\circ}\text{C}$ , then poured into water. An oily layer was separated, washed with water and dried over magnesium sulfate. This substance was subjected to analyses by glc and  $^{19}\text{F}$  nmr, which revealed that its composition was 94% 1-(p-methoxyphenoxy)pentafluoropropene with Z/E ratio 55/45 and 6% 1-(p-methoxyphenoxy)-1,1,2,3,3,3-hexafluoropropane, an HF-adduct of (1). On carrying out the reaction in dimethylformamide for 10 h, a product having similar Z/E ratio was obtained. In this case, however, the HF-adduct was formed in as much as 38% yield.

- 1 R. D. Chambers, Fluorine in Organic Chemistry, Wiley-Interscience, 1973, p.148.
- 2 R. D. Chambers and R. H. Mobbs, Advances in Fluorine Chemistry, Vol. 4, Butterworths, 1965, p.50.
- 3 N. Ishikawa and H. Harada, Nippon Kagaku Kaishi (1975) 3
- 4 W. A. Sheppard and C. M. Sharts, Organic Fluorine Chemistry Benjamin, 1969, p.31.