



Figure 2. Photostationary-state composition of 1,3-cyclooctadiene vs. time: ●, *cis,trans/cis,cis* starting with *cis,trans*-COD; □, *cis,trans/cis,cis* starting with *cis,cis*-COD.

ene from **2** at 25° is minimal. The photolysis was also carried out in a water-cooled cell at 10°. These conditions did not reduce the yield of bicyclo[4.2.0]oct-7-ene. These data indicate that bicyclo[4.2.0]oct-7-ene is a product of photolysis, and not the result of thermal isomerization of *cis,trans*-COD.

The 1,4 isomer from the photolysis solution, presumably resulting from a sigmatropic 1,3-hydrogen shift of the suprafacial type,¹⁴ was identified by gas chromatographic comparison with the authentic material. This was prepared by the reaction of lithium aluminum hydride with 1-bromo-2,4-cyclooctadiene.¹⁵

The nmr spectrum consisted of a multiplet from δ 6.1 to 5.0 (4 H) for the vinylic hydrogens, a multiplet between δ 2.9 and 2.5 (2 H) for the allylic hydrogens at the 3 position, a multiplet from δ 2.5 to 1.9 (4 H) for the allylic hydrogens at the 6 and 8 positions, and a multiplet from δ 1.7 to 1.1 (2 H) for the methylene hydrogens at the 7 position.

Three other components were also present in the mixture in a total yield of 7.3%. One of these, produced in 5.3% yield, showed a retention time near that of *cis*-bicyclo[4.2.0]oct-7-ene, and could be bicyclo[3.3.0]oct-2-ene.¹⁶ The other products were each present in approximately 1% yield.

Prolonged irradiation of *cis,cis*-COD results in a photostationary state between *cis,trans*-COD and *cis,cis*-COD with a *cis,trans/cis,cis* ratio of 0.60. This was verified by irradiating *cis,trans*-COD and observing the formation of

the photostationary state between **2** and **1** from the opposite direction. Figure 2 shows the formation of the photostationary state starting from *cis,cis*-COD and also from *cis,trans*-COD.

These data clearly point to a photostationary state between *cis,trans*-COD and *cis,cis*-COD.

Photochemical conversion of *cis,trans*-COD to bicyclo[4.2.0]oct-7-ene is excluded, as this would produce *trans*-bicyclo[4.2.0]oct-7-ene by a disrotatory¹⁷ process, and only *cis*-bicyclo[4.2.0]oct-7-ene was observed.

There is no evidence to indicate that bicyclo[4.2.0]oct-7-ene is formed by thermal isomerization of *cis,trans*-COD under the experimental conditions employed in this work. This, however, does not exclude the possibility that **3** could form from **2** if the *cis,trans* isomer were formed in the excited ground state from *cis,cis*-COD and isomerization to **3** occurred before vibrational relaxation were complete. Since the reaction was run in the liquid phase, this would be somewhat unique. This possibility of bicyclo[4.2.0]oct-7-ene being formed from the excited ground state, through a thermal conrotatory process and not directly from *cis,cis*-COD, is presently being investigated by studying the gas-phase photolysis of this system at various wavelengths.

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Fluorine Chemical Shifts of Substituted Aliphatic Monofluorides. Effect of Solvent

Sir:

We have found long-range ¹⁹F chemical shifts in fluoroalkanes substituted by electronegative groups in a position remote from the fluorine. Shielding effects as large as 3 ppm over six carbon atoms are observed when trifluoroacetic acid is used as solvent (see Table I). These long-range shifts should be compared with the enhanced long-range inductive effects found in solvolyses of fluoro-substituted tosylates¹ and are not observed in the non-polar solvent trichlorofluoromethane.

Fluorine-19 chemical shift measurements in aryl fluorides are valuable as a technique for studying a wide variety of substituent effects and intra- and intermolecular processes.^{2,3} However, the relative importance of the

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Table I. Substituent Chemical Shifts^a in Substituted 1-Fluoroalkanes

Compound	SCS ^a in solvent		$\Delta\delta$ (esterification)
	CFCl ₃	CF ₃ CO ₂ H	
CH ₂ OH(CH ₂) ₂ F	3.99	7.54	2.09
CH ₃ CHOH(CH ₂) ₂ F	2.50	6.44	1.72
CH ₃ CHOH(CH ₂) ₃ F	-0.51	2.75	1.63
CH ₃ CHOH(CH ₂) ₅ F	-0.21	1.61	0.50
CH ₃ CHOT(CH ₂) ₂ F	2.45	4.78	
CH ₃ CHOT ₃ (CH ₂) ₃ F	1.29	4.52	
CH ₃ CHOT ₃ (CH ₂) ₅ F	0.12	3.10	
CH ₂ (O ₂ CCF ₃)(CH ₂) ₂ F		9.63	
CH ₃ CH(O ₂ CCF ₃)(CH ₂) ₂ F		8.16	
CH ₃ CH(O ₂ CCF ₃)(CH ₂) ₃ F		4.38	
CH ₃ CH(O ₂ CCF ₃)(CH ₂) ₅ F		2.11	

^aPositive values for substituent chemical shifts (SCS) are expressed as parts per million upfield from the average value for 1-fluorohexane and 1-fluorodecane. The chemical shifts of these reference compounds in parts per million upfield from fluorotrichloromethane were found to be respectively: 219.22 (in CFCl₃), 212.41 (in CF₃CO₂H), 219.27 (in CFCl₃), and 212.59 (in CF₃CO₂H).

electrical effects of substituents on ¹⁹F shifts in aryl fluorides⁴ and more recently in alicyclic and bicyclic fluorides^{5,6} is a subject of controversy. A study of aliphatic fluorides potentially may resolve some of the issues involved. In methyl fluorides the expected deshielding effect is observed when the hydrogens of methyl fluoride are successively replaced by electronegative groups. However, in very recent studies of polycyclic and bicyclic molecules the effect of more remote electronegative substituents was a shielding effect in each instance.^{5,6}

The chemical shifts of our electronegatively substituted aliphatic monofluorides, calibrated on a Varian A-56/60 spectrometer, are given in Table I. Chemical shifts were obtained for 20, 10, and 5% solutions in fluorotrichloromethane or trifluoroacetic acid (containing 2% fluorotrichloromethane as internal reference) and extrapolated to infinite dilution. The column labeled $\Delta\delta$ (esterification) gives the difference in chemical shift between the alcohols (taken approximately 2 min after mixing with trifluoroacetic acid) and their corresponding trifluoroacetate esters formed by slow reaction with the solvent (taken after several hours). Any solvent effect of water upon chemical shifts should have been approximately nullified by extrapolation to infinite dilution.

The upfield (positive) shift with electron-withdrawing substituents, observed for most of our compounds, and also for the alicyclic and bicyclic fluorides,^{5,6} is not easily rationalized on the basis of empirical knowledge or theoretical predictions. That this shift for our compounds is not simply a function of chain length is indicated by a published study⁷ in which the chemical shift of the 1-fluoroalkanes from 1-fluoropropane through 1-fluoroheptane was found to vary by less than ± 0.4 ppm.

Representative substituent chemical shifts in nonpolar solvents for the bicyclooctanes⁶ and for selected examples of our compounds are compared in Table II. Anderson and Stock⁵ discussed the possible origin of their upfield

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Table II. Substituent Chemical Shifts of Acyclic and Bicyclic Fluorides

X	SCS ^a		X	SCS ^b	
	Acyclic	Bicyclic		Acyclic	Bicyclic
H	0.00		H	0.00	0.00
CO ₂ C ₂ H ₅	4.47		OH	-0.51	2.50
F	9.23		OSO ₂ C ₆ H ₄ CH ₃	1.29	2.45

^aParts per million in CCl₄. ^bParts per million in CFCl₃.

shifts, noting that "the positive SCS may be rationalized on the basis of the idea that there is an important repulsive interaction between the more electropositive bridgehead carbon atoms of the bicyclic molecules, leading to an elongation of the structure and an increase in the p character of the endocyclic carbon-carbon bonds." Although such an effect would indeed tend to pull the bicyclic C-C bonds (shown dark in the heading of Table II) nearer to 90°, it is not at all clear that a similar distortion of the C-C and C-H bonds (*cf.* Table II) in our acyclic compounds would occur. On the other hand, the remarkable ability of trifluoroacetic acid to increase the magnitude of substituent chemical shifts (*cf.* Table I) could be explained by changes in conformer populations and the attendant bond anisotropy effects. A possible explanation is that trifluoroacetic acid may hydrogen bond both to the oxygen-containing substituent⁸ and to the fluorine,⁹ increasing the mutual repulsion of the electronegative groups and increasing the population of elongated conformers.

Our preliminary results clearly point to the need for much more extensive studies of aliphatic fluorine chemical shifts in series of polar and nonpolar, protic and aprotic solvents, which should definitely include trifluoroacetic acid. Additional studies (by P. E. P.) are in progress.

(8) For references see P. E. Peterson, D. M. Chevli, and K. A. Sipp, *J. Org. Chem.*, **33**, 972 (1968).

(9) Moderately strong hydrogen bonding of phenol to aliphatic fluorine has been observed by R. West, D. L. Powell, L. S. Whately, M. K. T. Lee, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **84**, 3321 (1962).

(10) NASA Trainee, St. Louis University, 1964-1967. The research reported in this paper was supported in part by NASA Traineeship Grant NsG(T)-74 and in part by NSF 7 Grant GP291.

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A Symmetry Rule for Predicting Molecular Structure and Reactivity

Sir:

Symmetry considerations have proved to be a powerful means of predicting the course of certain chemical reactions. The Woodward-Hoffmann rules are outstanding