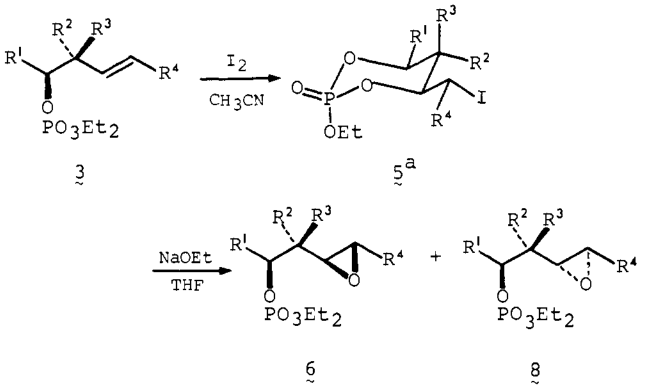
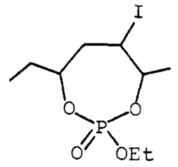
Table I. Epoxidation of Homoallylic Phosphates



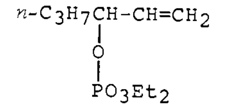
Series	Substituents	% yield of 7^b	% yield of $6 + 8^c$	Ratio, $6/8^d$
a	$R^1 = CH_3$; $R^2 = R^3 = R^4 = H$	87	75	>98:2
b	$R^1 = n\text{-}C_3H_7$; $R^2 = R^3 = R^4 = H$	85	75	>98:2
c	$R^1 = R^2 = CH_3$; $R^3 = R^4 = H$	80	72	95:5
d	$R^1 = R^3 = CH_3$; $R^2 = R^4 = H$	76	82	80:20
e	$R^1 = C_2H_5$; $R^2 = R^3 = H$; $R^4 = CH_3$	30	77	95:5

[a] Only the major isomer is depicted. [b] 2.2 equiv of I_2 in CH_3CN, 25 °C. [c] 1 equiv of NaOEt in THF, 0 °C. [d] Determined by ^{13}C NMR.

clization is still under investigation; however, preliminary evidence indicates that the seven-membered 1,3,2-dioxaphosphepane (**9**), a conceivable by-product,[10a,15] is not formed. An attempt to apply this strategy to epoxidation of the allylic phosphate **10** was not successful; treatment of this material with iodine in a variety of solvents failed to give any characterizable cyclic product.



9



$$n\text{-}C_3H_7\underset{\substack{|\\ O\\ |\\ PO_3Et_2}}{CH}\text{-}CH{=}CH_2$$

10

Intramolecular participation of an appropriately placed nucleophile promises to be a useful strategy in the stereocontrolled synthesis of acyclic systems, because it is an effective way to reduce the conformational mobility and to increase the free-energy difference of diastereomeric transition states. In this overall epoxidation sequence, the phosphoryl group serves two purposes: it extends the nucleophilic character of the hydroxyl group in a useful manner and it is a bulky, achiral unit which maximizes the steric constraints on the cyclic intermediate. As a result, this derivative of the homoallylic alcohols can be epoxidized with 1,3-asymmetric induction with selectivities which are unprecedented for such acyclic substrates.

Acknowledgment. Support for this research was provided by the National Cancer Institute (Grant No. CA-16616) and through Departmental Equipment Grants (GP-32796 and CHE 76 05512), the National Science Foundation.

References and Notes

(1) (a) S. Masamune, C. V. Kim, K. E. Wilson, G. O. Spess, P. E. Giorghiou, and G. S. Bates, *J. Am. Chem. Soc.*, **97**, 3512 (1975); S. Masamune, H. Yamamoto, S. Kamata, and A. Fukuzawa, *ibid.*, **97**, 3513 (1975); (b) A. I. Meyers, C. C. Shaw, D. Horne, L. M. Trefonas, and R. J. Majeste, *Tetrahedron Lett.*, 1745 (1975); A. I. Meyers and R. Brinkmeyer, *ibid.*, 1749 (1975); (c) E. J. Corey and M. G. Bock, *ibid.*, 2643 (1975); (d) W. A. Court, O. E. Edwards, C. Grieco, W. Rank, and T. Sano, *Can. J. Chem.*, **53**, 463 (1975); (e) H. Gerlach, K. Oertle, A. Thalmann, and S. Servi, *Helv. Chim. Acta*, **58**, 2036 (1975); U. Schmidt, J. Gombos, E. Haslinger, and H. Zak, *Ber.*, **109**, 2628 (1976); G. Beck and E. Henseleit, *ibid.*, **104**, 21 (1971); (f) M. Miljković, M. Gligorijević, T. Satoh, and D. Miljković, *J. Org. Chem.*, **39**, 1379 (1974).

(2) (a) Reviews: J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions", Prentice-Hall, Englewood Cliffs, N.J., 1971; H. Pracejus, *Fortschr. Chem. Forsch.*, **8**, 493 (1967); D. R. Boyd and M. A. McKervey, *Quart. Rev.*, **22**, 95 (1968); J. Mathieu and J. Weill-Raynal, *Bull. Soc. Chim. Fr.*, 1211 (1968). (b) 1,2-Asymmetric induction, inter alia: R. Auerbach and C. A. Kingsbury, *Tetrahedron*, **29**, 1457 (1975) and references therein; S. B. Bowlus and J. A. Katzenellenbogen, *J. Org. Chem.*, **39**, 3309 (1974); A. Goset et al., *J. Appl. Chem. Biotechnol.*, **25**, 1, 13, 19 (1975); D. R. Dimmel and S. Huang, *J. Org. Chem.*, **38**, 2756 (1973). (c) 1,3-Asymmetric induction, inter alia: T. J. Leitereg and D. J. Cram, *J Am. Chem. Soc.*, **90**, 4019 (1968); J. Michel and P. Canonne, *Can. J. Chem.*, **49**, 4084 (1971); C. Fouquey, J. Jacques, L. Angiolini, and M. Tramontini, *Tetrahedron*, **30**, 2801 (1974), and references therein.

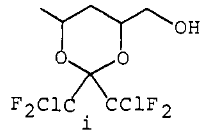
(3) (a) P. Chautemps and J.-L. Pierre, *Tetrahedron*, **32**, 549 (1976); (b) S. Tanaka, H. Yamamoto, H. Nozaki, K. B. Sharpless, R. C. Michaelson, and J. D. Cutting, *J. Am. Chem. Soc.*, **96**, 5254 (1974).

(4) G. Berti *Top. Stereochem.*, 7, 93 (1973).

(5) E. J. Corey and M. G. Bock, *Tetrahedron Lett.*, 2643 (1975).

(6) All compounds discussed are racemic, although only one enantiomer of each is depicted.

(7) V. I. Pansevich-Kolyada and T. A. Galysheva, *Vestsi Akad. Navuk B. SSR, Ser. Khim. Navuk*, 89 (1971); *Chem. Abstr.*, **74**, 140817 (1971). The relative configurations of the epoxy alcohols were assigned by conversion to the hexahaloacetonides i (**2t** → *cis*-i, **2e** → *trans*-i) using $CClF_2C(=O)CClF_2$/NaH, followed by comparison with materials of known configuration.[8]



(8) P. A. Bartlett, unpublished work.

(9) D. L. H. Williams, E. Bienvenüe-Goetz, and J. E. Dubois, *J. Chem. Soc. B*, 517 (1969); see also V. I. Staninets and E. A. Shilov, *Russ. Chem. Rev.*, **40**, 272 (1971).

(10) The use of chloral and fluoral to extend the nucleophilicity of a hydroxyl group is an alternative strategy which has been described: (a) L. E. Overman and C. B. Campbell, *J. Org. Chem.*, **39**, 1474 (1974); (b) G. Stork, C. Kowalski, and G. Garcia, *J. Am. Chem. Soc.*, **97**, 3258 (1975).

(11) L. D. Hall and R. B. Malcolm, *Can. J. Chem.*, **50**, 2102 (1972).

(12) J.-P. Majoral and J. Narech, *Spectrochim. Acta, Ser. A*, **28**, 2247 (1972).

(13) C. E. McKenna, M. T. Higa, N. H. Cheung, and M.-C. McKenna, *Tetrahedron Lett.*, 155 (1977).

(14) The relative stereochemistry of the isomeric 3-methyl-4-penten-2-ols was assigned by 180-MHz ^1H NMR analysis of the cyclic phosphates **5c** and **5d**.

(15) Satisfactory analytical and spectral characterization was obtained for all new compounds.

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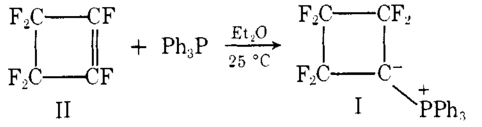
Trialkylammonium-2,2,3,3,4,4-hexafluorocyclobutane Ylides.[1] Preparation and Isolation of an Unusually Stable Fluorinated Carbanion

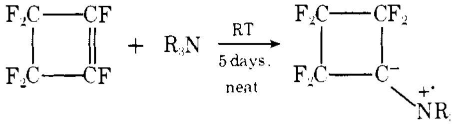
Sir:

The first reported example of a stable polyhalogenated phosphonium ylide was 2,2,3,3,4,4-hexafluoro(triphenylphosphoranylidene)cyclobutane (I), which was obtained from the reaction of hexafluorocyclobutene (II) with triphenylphosphine.[2,3] Ylide (I) is a rare example of an isolable fluorinated carbanion. The remarkable stability of I was attributed to the overlap of the phosphorus d orbitals with the ylide carbon p orbitals and the strong inductive effect of the adjacent difluoromethylene groups.[6] However, in this case it was difficult to assess the relative importance of the inductive effect of the



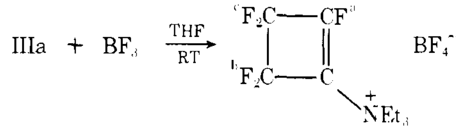
adjacent difluoromethylene groups toward stabilization of I.

We now wish to report the first example of an isolable fluorinated carbanion uncomplicated by dπ–pπ types of interactions. When I is allowed to react with trialkylamines, the stable polyfluorinated carbanion, the trialkylammonium-2,2,3,3,4,4-hexafluorocyclobutane ylide (III), is formed. Ylide



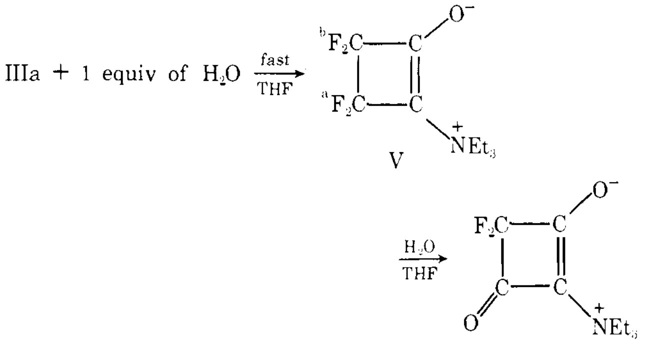
IIIa, R = Et, 80%
b, R = n-Bu, 55%

IIIa is a pale yellow, moisture-sensitive solid, which, except for the one missing doublet splitting (due to phosphorus), shows a ^{19}F NMR spectrum similar to that of I.[7] It exhibits two sets of multiplets at ϕ^* 85.5 (rel area 2) and 122.4 ppm (rel area 1).[8] The spectroscopic data is only consistent with the ylide structure III. It is totally inconsistent with the earlier suggested ammonium salt structures for the products of these reactions.[9] A derivative of the cyclobutenylammonium structure was prepared for spectroscopic comparison purposes. For example, when IIIa was treated with boron trifluoride etherate, 1-(pentafluorocyclobutenyl)triethylammonium tetrafluoroborate (IV) was formed in quantitative yield. Salt IV is a moisture-sensitive solid which exhibits the following ^{19}F NMR spectrum, ϕ^* 95.8 (rel area 1, F^a), 112.4 (rel area 2, F^b), 119.2 (rel area 2, F^c), and 153.3 ppm (rel area 4, BF$_4^-$), in agreement with the postulated structure.



IV

The hydrolysis of IIIa can be carried out sequentially to give either a mono (V)[10] or bis (VI)[11] hydrolysis product. Compound VI is identical with the hydrolysis product isolated by Rapp,[12] providing corroborative evidence that our compound III is the same as reported earlier.



VI, 78%

Confirmation of our spectroscopic conclusions above has been recently provided by an x-ray structural determination of IIIb.[13] The x-ray determination unequivocally shows the ylidic structure, rather than the ammonium salt, to be the correct representation of III. To our knowledge, III is the first reported example of a stable halogenated nitrogen ylide and the first example of a stable fluorinated carbanion system stabilized only by inductive effects.

The ease of formation and stability of III suggests that other related polyfluorinated carbanion systems may be similarly formed and exhibit inherent stability, even in the absence of any dπ–pπ stabilization.[14] Sufficient inductive stabilization can decrease the ease of the usually favored β-elimination process and permit the formation and isolation and study of unusual carbanion systems. Our work continues to explore these unusual elusive carbanions.

References and Notes

(1) Reported in part at the 8th International Symposium on Fluorine Chemistry, 1976, Kyoto, Japan.

(2) M. A. Howells, R. D. Howells, N. C. Baenziger, and D. J. Burton, *J. Am. Chem. Soc.*, **95**, 5366 (1973).

(3) Related fluorinated phosphoranes capable of isolation have also been reported by Middleton[4] and Matthews.[5]

(4) W. J. Middleton and W. H. Sharkey, *J. Org. Chem.*, **30**, 1384 (1965).

(5) G. H. Birum and C. N. Matthews, *J. Org. Chem.*, **32**, 3554 (1967).

(6) The phosphorus-carbon bond length of 1.713 Å[2] was indicative of dπ–pπ overlap. When halogens other than fluorine were substituted at the position α to the ylide carbon, the stability of the ylide decreased, suggesting that partial stabilization came from the α-difluoromethylene groups.

(7) Ylide I exhibits two sets of signals in the ^{19}F NMR at ϕ^* 86.9 (4 F) and 124.6 ppm (2 F).

(8) Ylide IIIb shows a similar ^{19}F NMR pattern at ϕ^* 84.1 (4 F) and 122.8 ppm (2 F).

(9) R. L. Pruett, C. T. Bahner, and H. A. Smith, *J. Am. Chem. Soc.*, **74**, 1633 (1952).

(10) V shows two triplets in the ^{19}F NMR at ϕ^* 102.6 (F^a) and 122.5 ppm (F^b) with $J_{F,F}$ = 21 Hz.

(11) VI shows a singlet in the ^{19}F NMR spectrum at 120.7 ppm and mp 166–167 °C (lit.[12] mp 167–167.5 °C).

(12) K. E. Rapp, *J. Am. Chem. Soc.*, **73**, 5901 (1951).

(13) The x-ray structure of IIIb was carried out by Professor Norman Baenziger (University of Iowa) and will be reported elsewhere.

(14) For earlier work with pyridine and pyridine derivatives, see R. L. Pruett, C. T. Bahner, and H. A. Smith, *J. Am. Chem. Soc.*, **74**, 1638 (1952); S. E. Ellzey and W. A. Guice, *J. Org. Chem.*, **31**, 1300 (1966); and R. F. Stockel and F. H. Megson, *Can. J. Chem.*, **45**, 1998 (1967).

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Comments on Entropy Change in Ion–Molecule Equilibria

Sir:

In recent years, many investigators have reported quantitative information about the thermochemistry of ion-molecule reactions based on the observation of ion-molecule equilibria in high pressure or ion cyclotron resonance mass spectrometers. Such equilibria have been observed in systems in which hydride transfer,[1] proton transfer,[2] and charge transfer[3] reactions occur reversibly. In some of these investigations, the equilibrium constant is determined as a function of temperature, thus giving an experimental determination of the entropy change for the reaction. Thus a value for the enthalpy can be obtained:

$$-RT \ln K_{eq} = \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (1)$$

However, in many studies, K_{eq} is determined at a single temperature only. In many such investigations the results are interpreted in terms of enthalpy changes by making the assumption that the entropy change is zero, or can be estimated entirely on the basis of the differences in symmetry, moments of inertia, vibrational frequencies, and degeneracies of the electronic states of the reactant and product species. On this basis, scales of "proton affinities" and scales of "adiabatic ionization potentials" have been reported which often have an estimated accuracy of ±0.1 or 0.2 kcal/mol (1 kcal/mol = 4.18 kJ = 0.043 eV). In this communication, it will be shown that, when eq 1 is used for the derivation of thermodynamic information from ion-molecule equilibrium constants, terms must be included to account for the effects of the intermolecular forces experienced by the ions and molecules which undergo reaction. The contribution to the entropy change due to the