(62% from 11a) as yellow needles: mp 124–125 °C; ^{1}H NMR ($CDCl_3$) δ 7.2–7.8 (m, 3 H), 4.25 (q, 4 H, J = 7 Hz), 4.05 (s, 3 H), 3.9 (s, 3 H), 3.3 (s, 2 H), 2.9 (t, 2 H, J = 6 Hz), 2.3 (t, 2 H, J = 6 Hz), 1.3 (t, 6 H, J = 7 Hz). The conversion of **14a** into 7,9-dideoxydaunomycinone dimethyl ether (**17a**) was then effected by the following four-part procedure.

Saponification (KOH, aqueous ethanol (1:2), 90 °C, 3 h, 98%) of **14a** led to the diacid **15a** as yellow needles, mp 222–224 °C from CH_2Cl_2/Et_2O. This was the decarboxylated (CH_3CO_2H, piperidine, 120 °C, 1 h) to give monocarboxylic acid **16a** (85% from **14a**): mp 133.5–135 °C; ^{1}H NMR (acetone-d_6) δ 7.6–7.9 (m, 3 H), 4.1 (s, 3 H), 4.0 (s, 6 H), 2.7–3.1 (m, 7 H), ~9 (very br, 1 H). The crude acid chloride derived ($SOCl_2$, C_6H_6, 25 °C, 15 h) from **16a** was then treated with lithium dimethylcuprate[15] (THF/Et_2O, −78 to 0 °C, 3 h) and afforded 7,9-dideoxydaunomycinone dimethyl ether (**17a**, 80% based on **16a**) as yellow needles: mp 185–186 °C; ^{1}H NMR (acetone-d_6) δ 7.6–7.9 (m, 3 H), 4.1 (s, 3 H), 3.9 (s, 6 H), 2.8–3.1 (m, 7 H), 2.3 (s, 3 H).

Selective demethylation of **17a** to give *dl*-7,9-dideoxydaunomycinone (**3**) was possible only by a two-part sequence, namely oxidation[6b,16] (AgO/HNO_3, aqueous acetone, 70 °C, 1 h) to the 4,12:6,11-bisquinone, followed by reduction (Et_2NOH, EtOAC, 25 °C, 30 min) of the crude product. This afforded **3** in 83% yield after recrystallization from CH_2Cl_2/Et_2O: mp 243–245 °C, no depression in melting point when admixed with an authentic sample (mp 243–245 °C); ^{1}H NMR ($CDCl_3$) δ 13.78 (s, 1 H), 13.43 (s, 1 H), 8.1–7.2 (m, 3 H), 2.27 (s, 3 H), 2.15 (m, 1 H), 1.55 (m, 2 H). The NMR, IR (Nujol), visible (CH_2Cl_2), and mass spectra were identical with those recorded in the literature[8a] for **3**.

Although the demethylation of **17a** is an efficient process, the initial oxidation is rather vigorous and one could envisage that more delicate molecules may not survive. To avoid this difficulty we have developed an alternative procedure based on the fact that aryl ethyl ethers are more readily cleaved[17] by Lewis acids than the corresponding methyl ethers. Repetition then, of the complete synthetic sequence[18] starting with **6b** produced in comparable yields the corresponding diethoxy homologues **7b** through **17b**. Selective deethylation of **17b** to give **3** was then easily accomplished in one step under mild conditions ($AlCl_3/PhNO_2$, 45 °C, 40 min, 80%).

We believe that the methods presented above, together, constitute a very versatile approach to the anthracyclinones in general. Variations in the substitution patterns of rings A, B, and D and in the nature of the C-9 side chain now seem possible, not only because of the convergent nature of the synthesis and its regiospecificity but also because of the relatively simple nature of the reactions involved. Investigations into the use of these procedures for the synthesis of other classes of anthracyclinones are underway.

Acknowledgment. The authors are grateful to Dr. F. Arcamone (Farmitalia) for a generous financial gift in support of the research. The project was also partially supported by grants from the National Cancer Institute (Grant CA20197) and from the State University of New York. The technical assistance of Mr. John Winter, Mr. Michael W. Spatz, and Miss Nancy Stambler is acknowledged.

Reference and Notes

(1) K. S. Kim, M. W. Spatz, and Francis Johnson, *Tetrahedron Lett.*, 331 (1979).
(2) H. Brockmann, *Prog. Chem. Org. Nat. Prod.*, **21**, 121 (1963).
(3) (a) F. Arcamone, G. Cassinelli, G. Fantini, A. Grein, P. Orezzi, C. Pol, and C. Spalla, *Biotechnol. Bioeng.*, **11**, 1101 (1969); (b) F. Arcamone, G. Franceschi, P. Orezzi, G. Cassinelli, W. Barbiere, and R. Mondelli, *J. Am. Chem. Soc.*, **86**, 5334 (1964).
(4) A. DiMarco, M. Gaetani, and B. Scarpinato, *Cancer Chemother. Rep.*, **53**, 33 (1969).
(5) D. W. Henry in "Cancer Chemotherapy", A. C. Sartorelli, Ed., American Chemical Society, Washington, D.C., 1976, Chapter 2.
(6) (a) C. M. Wong, R. Schwenk, D. Dopien, and T. L. Ho, *Can J. Chem.*, **51**, 466 (1973); (b) A. S. Kende, Y. G. Tsay, and J. E. Mills, *J. Am. Chem. Soc.*, **98**, 1967 (1976).
(7) (a) P. W. Reynolds, M. J. Manning, and J. S. Swenton, *Tetrahedron Lett.*, 2383 (1977); J. S. Swenton and P. W. Reynolds, *J. Am. Chem. Soc.*, **100**, 6188 (1978). (b) F. Suzuki, S. Trenbeath, R. D. Gleim, and C. J. Sih, *ibid.*, **100**, 2272 (1978).
(8) (a) R. D. Gleim, S. Trenbeath, R. S. D. Mittal, and C. J. Sih, *Tetrahedron Lett.*, 3385 (1976); (b) F. Arcamone, G. Franceschi, and S. Penco, U.S. Patent 3 803 124 (1974).
(9) Details of other research work which shows that the 3-phthalido group does indeed have an electron-withdrawing effect may be found in part 1 of this series.[1] However, the effect, in part at least, can be equated with the substitution of chlorine or acetoxy in the α position of an aralkane which leads to diminished reactivity of the aromatic ring toward electrophilic substitution. This is well illustrated for example, by the fact that chloromethylmesitylene is **46** times less reactive than mesitylene itself toward chloromethylation: G. Vavon, J. Bolle, and J. Calin, *Bull. Soc. Chim. Fr.*, **6**, 1025 (1930). The coordination of the Friedel–Crafts catalyst with the lactone of the product probably also makes a contribution to the diminished reactivity of the aromatic ring.
(10) C. A. Buehler, T. A. Powers, and J. G. Michels, *J. Am. Chem. Soc.*, **66**, 417 (1944).
(11) Suitable analytical data were obtained for all new compounds discussed in this paper.
(12) The base-induced opening of the lactone is competitive with the hydrolysis of the methyl ester. However, the former reaction appears to be a reversible reaction so that, with considerably less than 2 equiv of base, the desired ester hydrolysis goes to completion.
(13) It should be noted that the presence of the two ethyl esters on the side chain is essential to good yields in this reaction. In the analogous compound having only one ester group at this position, cyclization with this reagent cannot be induced. This appears to be an outstanding example of the effects of B strain: H. C. Brown, H. Bartholamy, and M. D. Taylor, *J. Am. Chem. Soc.*, **94**, 5106 (1972). For another example, see E. Testa and L. Fontanella, *Justus Liebigs Ann. Chem.*, **625**, 94 (1959).
(14) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).
(15) G. H. Posner, C. E. Whitten, and P. E. McFarland, *J. Am. Chem. Soc.*, **94**, 5106 (1972).
(16) C. D. Snyder and H. Rapoport, *J. Am. Chem. Soc.*, **94**, 277 (1972).
(17) C. Szantáy, *Acta Chim. Acad. Sci Hung.*, **12**, 83 (1957).
(18) The 1,4-diethoxybenzene needed for this synthesis is easily obtained (88%) by the ethylation of hydroquinone (Et_2SO_4/KOH, H_2O–CH_2Cl_2, Pr_4, NOH, 25 °C, 36 h). Formylation (Cl_2CHOCH_3, $SnCl_4$, CH_2Cl_2, 0 °C, 20 min) then yields 2,5-diethoxybenzaldehyde (85%). Conversion of the latter into **6b** follows exactly the three-step procedure (93% overall) used for **6a**, namely condensation with diethyl malonate, catalytic reduction (H_2, Pd/C, EtOAc), and alkylation with methyl bromoacetate (NaH, C_6H_6, 25 °C). The melting points (°C) of the **b** series are as follows: 2,5-diethoxybenzaldehyde, 60–61; diethyl 2,5-diethoxybenzylidenemalonate 52–53; **7b**, 122–126; **8b**, 150–151; **9b**, 111–113; **11b**, 110–111; **14b**, 111–113; **15b**, 198–200 dec; **16b**, 213–214; **17b**, 147.

K. S. Kim, Ermes Vanotti
Antonino Suarato, Francis Johnson*
Departments of Pharmacological Sciences and Chemistry
State University of New York at Stony Brook
Stony Brook, New York 11794
Received September 20, 1978

2-Hydroperoxyhexafluoro-2-propanol. A Low-Cost, Catalytic Oxidant for Synthesis and a Structural Analogue of Naturally Occurring Flavin Hydroperoxides

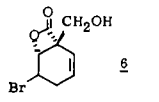
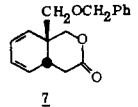
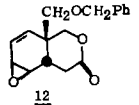
Sir:

Organic chemists have long been interested in utilizing hydrogen peroxide directly for the epoxidation of simple, unactivated alkenes. Efforts to devise a workable process using H_2O_2 to drive the carboxylic acid–peracid exchange have been unsuccessful to date since a strong acid catalyst is required.[1] Transition metal oxides and peroxides achieve a ready equilibrium but are poor oxidants for isolated double bonds.[2] Only recently have the corresponding seleninic–peroxyseleninic acid systems been described as satisfactory alternatives, although they offer little, if any, regio- or stereoselectivity.[3,4]

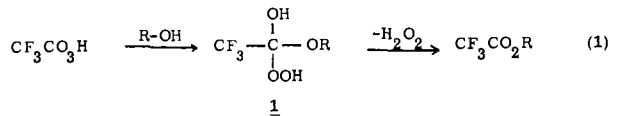
Since our discovery[5] that peroxytrifluoroacetic acid esterifies alcohols by a Fischer-type mechanism (eq 1), we have been exploring the chemistry of electron-deficient hydroperoxides related to **1**. We now report that 2-hydroperoxyhexafluoro-

0002-7863/79/1501-2484$01.00/0

Table I. Stoichiometric Epoxidation of Alkenes with 2

Alkene	Equiv. of 2	Time (Temp)[a]	Product (Yield)[e]
1-dodecene	1.1	6h (rt)	1,2-epoxydodecane (93%)
cyclododecene	1.2	5h (rt)	epoxycyclododecane (96%)
cholesterol	1.2	10h (rt)	5α,6α-epoxycholesterol 8[b] (70%) 5β, 6β-epoxycholesterol (25%)
cyclohexene	1.0	15 min (0° → rt)	epoxycyclohexane (90%)
2-cyclohexenone	1.0	12h (rt) 4h (reflux)	N. R.
2-cyclohexen-1-ol 4	1.0	22h (rt)	9  (90% distilled)
(2-cyclohexenyl)acetate 5	1.2	15h (reflux)	10 (75%)  11 
tetramethylethylene	1.2	30 min (0°)	$(CH_3)_2C$—O—$C(CH_3)_2$ (60%)[d]
 6	1.2	3h (rt) 48h (reflux)	N. R.
 7	1.2	12h (rt)	 12 90%

[a] The hydroperoxide was added to solutions of each alkene (0.7–1.0 M in CH_2Cl_2) at 0 °C and then brought to the indicated reaction temperature. [b] This yield represents pure, recrystallized product. [c] The stereochemistry of **9** was assayed as its acetate; see ref 14. [d] This low yield is largely due to product volatility. [e] Products can be isolated in quite high purity simply by washing the reaction mixture with aqueous sodium thiosulfate and sodium carbonate to remove residual **2** and **3**.

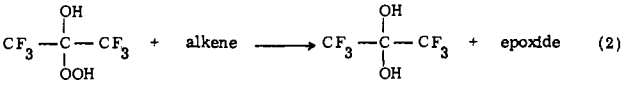


(1)

1

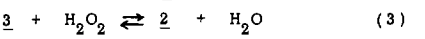
2-propanol (**2**, HPHI) is a reactive oxidizing agent possessing considerable selectivity of value to the synthetic chemist and displaying remarkable parallels in structure and function with biologically active flavin oxidants. Moreover the byproduct of oxidation, hexafluoroacetone hydrate (**3**), readily disproportionates with H_2O_2 to regenerate **2**, thereby implementing a simple catalytic cycle.

Hydroperoxide **2**, prepared as a neat liquid in 1971 by the reaction of hexafluoroacetone with concentrated H_2O_2,[6] de-



(2)

2 **3**



(3)

composes at room temperature to form CO_2, CF_3OOH, O_2, and other products. Solutions of **2** have been shown to effect the Baeyer–Villiger oxidation of simple ketones at elevated temperature, but little else is known about its chemistry.[7] We reasoned that **2** ought to epoxidize alkenes since it shares many of the structural features of peroxyimidic,[8] peroxycarbamic,[9] and peroxycarboxylic acids. Moreover the weak acidity of hexafluoroacetone hydrate (pK_A of **3** = 6.76[10]) should permit isolation of all but the most sensitive epoxide products. In fact, when a 1 M CH_2Cl_2 solution of **1**-dodecene is treated with 1.1 equiv of **2** at room temperature for 6 h, 1,2-epoxydodecane is produced in 93% yield. Similar results with a variety of representative alkenes are presented in Table I. We have found it most convenient for routine, small-scale use to prepare 0.5–1.0 M solutions of **2** in CH_2Cl_2 which, when stored at −5 °C, maintain their activity with negligible changes in titer for up to 2 months.[11] Even boiling for 4 h caused no measurable decomposition, indicating the enhanced stability of **2** in dilute halocarbon solution. As expected, electron-deficient alkenes such as 2-cyclohexenone resist oxidation even at reflux, as does the severely hindered olefinic lactone **6** which has only been epoxidized successfully with CF_3CO_3H.[12] Although Chambers and Clark report that 2-hydroperoxyhexafluoro-2-propanol is capable of oxidizing ketones to esters and lactones,[7a] our own experiments with **2** have revealed that such Baeyer–Villiger reactions are actually quite sluggish at ambient temperature. For example, exposure of cyclohexanone to **2** for 6 h produces mere traces of caprolactone. In this respect, the selectivity of **2** as an epoxidizing agent in polyfunctional systems is superior to commonly used oxidants such as *m*-chloroperoxybenzoic acid (MCPBA).

Another singular characteristic of **2** is its exceptional stereoselectivity in the epoxidation of allylically oxygenated alkenes. Whereas 2-cyclohexen-1-ol (**4**) furnishes a 93:7 mixture of *cis,trans*-epoxycyclohexanol with MCPBA,[13] oxidation with **2** forms only the cis isomer **9**, within the limits of GLC detection.[14] Cyclohexenyl acetate (**5**) is oxidized more slowly (reflux, CH_2Cl_2) and when carried to completion the reaction affords only *cis*-epoxyacetate **10** in 75% yield along with more polar byproducts. This apparently exclusive syn-epoxidation is an artifact: control experiments reveal that the trans isomer **11** is selectively and rapidly hydrolyzed under the conditions of oxidation. When the epoxidation of **5** with **2** is run only to 10% completion, an 80:20 ratio of **10**:**11** is observed. This selectivity is still considerably superior to the oxidation of **5** with MCPBA (**10**:**11**, 40:60). An additional measure of the uniqueness of **2** is evident from the regio- and stereoselectivity it displays in the epoxidation of **7**. This bicyclic diene gives rise to all four possible monoepoxides when subjected to a variety of peracids, transition metal hydroperoxides, and singlet oxygen–trimethyl phosphite.[12] In contrast, oxidation of **7** with

Table II. Catalytic Epoxidation of Alkenes with **2** and H_2O_2

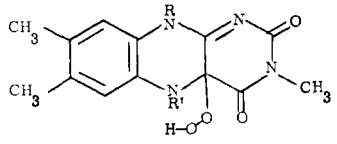
alkene (mmol)	catalyst (mol %)	oxidant	conditions	product (yield, %)
1-dodecene (15)	**2** (13)	90% H_2O_2 (2 equiv)	CH_2Cl_2, reflux, 72 h	1,2-epoxydodecane (77) 1-dodecene (20)
1-dodecene (7)	**2** (14)	90% H_2O_2 (2 equiv)	1:1 EtOAc–CH_2Cl_2,[a] reflux, 24 h	1,2-epoxydodecane (25) 1-dodecene (75)
1-dodecene (7)	**3** (14)	90% H_2O_2 (2 equiv)	$ClCH_2CH_2Cl$, reflux, 21 h	1,2-epoxydodecane (85)
1-dodecene (60)	**2** (14)	90% H_2O_2 (2 equiv)	$ClCH_2CH_2Cl$, reflux, 24 h	1,2-epoxydodecane (91, distilled)
cyclododecene (60)	**2** (13)	90% H_2O_2 (2 equiv)	$ClCH_2CH_2Cl$, reflux, 24 h	epoxycyclododecane (92, distilled)

[a] These conditions afford a homogeneous solution.

2 generates **12** as the only product in high yield.[15]

By taking advantage of the equilibrium described in eq 3, it is also possible to perform epoxidations which are catalytic in **2**. This is an attractive alternative for large-scale operations when it is desirable to avoid the handling and expense of preformed, stoichiometric quantities of **2**. The procedure involves a two-phase mixture of substrate, solvent, excess H_2O_2, and 10–15 mol % of either **2** or **3**.[16] Since the disproportionation of H_2O_2 with **3** is rather slow at room temperature,[17] these oxidations are conveniently run in 1,2-dichloroethane at reflux. The synthesis of epoxides by the catalytic method is summarized in Table II. Although 90% H_2O_2 gives the best results, 30% solutions of the oxidant can be substituted with only minor diminution in overall rate. Runs using 30% H_2O_2 could be accelerated somewhat by adding anhydrous $MgSO_4$, but the effect is not pronounced.

The electronic structure of **2** bears some similarity to the oxidized 4a-flavin hydroperoxides of type **13** which have been implicated in epoxidations and hydroxylations by external flavoprotein monooxygenases[18,19] and in the bioluminescence of bacterial luciferase.[20] The central hydroperoxide in both **2**



13

and **13** is flanked by electron-withdrawing substituents and lies adjacent to a weakly basic, electronegative group (OH, PhNH). Like the native coenzymes, HPHI does hydroxylate arenes; mesitylene reacts with **2** to produce mesitol in 40% yield.[4a] The chemiluminescent event in bacterial luciferase has been shown by Hastings[21] to involve the combination of **13** with some endogenous aldehyde leading to a chemically excited state. Although mechanistic details are sketchy,[22] a carboxylic acid ultimately arises from the aldehyde component. Consistent with this picture, we found that *n*-heptanal formed heptanoic acid (90% yield) when treated with 1 equiv of HPHI (CH_2Cl_2, reflux, powdered Na_2CO_3). Since alcohols are inert to **2**, this selective aldehyde oxidation could prove valuable in complex synthetic manipulations.

We are continuing to explore these heretofore unrecognized flavin mimics and the mechanisms by which they operate.

Acknowledgment. We thank the National Institutes of Health for generous financial support.

References and Notes

(1) S. N. Lewis in "Oxidation", Vol. 1, R. L. Augustine, Ed., Marcel Dekker, New York, 1969, p 216.
(2) (a) G. B. Payne and P. H. Williams, *J. Org. Chem.*, **24**, 54 (1959); (b) H. C. Stevens and A. J. Kamens, *J. Am. Chem. Soc.*, **87**, 734 (1965).
(3) P. A. Grieco, Y. Yokoyama, S. Gilman, and M. Nishizawa, *J. Org. Chem.*, **42**, 2035 (1977).
(4) T. Hori and K. B. Sharpless, *J. Org. Chem.*, **43**, 1689 (1978).
(5) G. W. Holbert and B. Ganem, *J. Chem. Soc., Chem. Commun.*, 248 (1978).
(6) (a) C. T. Ratcliffe, C. V. Hardin, L. R. Anderson, and W. B. Fox, *J. Chem. Soc., Chem. Commun.*, 784 (1971); (b) U.S. Patent 1 288 706 (1971).
(7) (a) R. D. Chambers and M. Clark, *Tetrahedron Lett.*, 2741 (1970); (b) L. Kim, Ger. Offen. 2 239 681 (to Shell).
(8) G. B. Payne, *Tetrahedron*, **18**, 763 (1962).
(9) (a) J. Rebek, Jr., S. F. Wolf, and A. B. Mossman, *J. Chem. Soc., Chem. Commun.*, 711 (1974); (b) *J. Org. Chem.*, **43**, 180 (1978).
(10) J. Hine and N. W. Flachskam, *J. Org. Chem.*, **42**, 1979 (1977).
(11) At lower temperatures the hydroperoxide is insoluble in CH_2Cl_2 and forms a separate liquid phase.
(12) G. W. Holbert and B. Ganem, *J. Am. Chem. Soc.*, **100**, 352 (1978).
(13) H. B. Henbest and R. A. L. Wilson, *J. Chem. Soc.*, 1958 (1957).
(14) GLC analyses of the corresponding acetates were performed on a 6-ft column of 10% DEGS on 80/100 Gas-Chrom A; retention times for the cis isomer **10** and trans isomer **11** are 4.5 and 3.5 min, respectively, at 159 °C.
(15) We thank Professor Robert K. Boeckman, Jr., of Wayne State University for informing us of his results with **2** prior to publication.
(16) Hexafluoroacetone hydrate is commercially available from either Aldrich or Sigma Chemical Co.
(17) This is not simply the result of poor mixing in these two-phase systems: using a homogeneous medium of 1:1 ethyl acetate–CH_2Cl_2 causes no increase in the rate of epoxidation.
(18) G. A. Hamilton in "Progress in Bioorganic Chemisty", Vol. 1, E. T. Kaiser and F. J. Kézdy, Eds., Wiley-Interscience, New York, 1971, pp 83–157.
(19) V. Massey and P. Hemmerich in "The Enzymes", Vol. 12 P. D. Boyer, Ed., Academic Press, New York, 1976 pp 191–252.
(20) F. McCapra, *Acc. Chem. Res.*, **9**, 201 (1976).
(21) J. W. Hastings, C. Balny, C. Le Peuch, and P. Douzou, *Proc. Natl. Acad. Sci. U.S.A.*, **70**, 3468 (1973).
(22) C. Kemal and T. C. Bruice, *Proc. Natl. Acad. Sci. U.S.A.*, **73**, 995 (1976).
(23) Fellow of the A. P. Sloan Foundation, 1978–1980; Recipient of a Camille and Henry Dreyfus Teacher-Scholar Grant, 1978–1983.

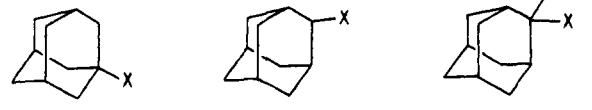
Richard P. Heggs, Bruce Ganem*[23]
Department of Chemistry, Cornell University
Ithaca, New York 14853
Received January 11, 1979

S_N2 Character of Solvolyses of *tert*-Butyl Halides and of Trifluoroacetolyses of Secondary Alkyl Sulfonates

Sir:

The importance of nucleophilic solvent assistance[1] is now well established for many solvolyses, e.g., simple secondary alkyl sulfonates[2-6] and β-aryl systems.[7] We now report evidence for two additional, important, and unexpected cases of significant nucleophilic solvent assistance: (1) solvolyses of *tert*-butyl halides, key reference points for structural[8] and medium effects[9] on the reactivity of organic systems; (2) trifluoroacetolyses of simple secondary alkyl sulfonates, previously assumed to be S_N1 (limiting) reactions and used as reference points for minimum estimates of nucleophilic solvent assistance in more nucleophilic media.[2,4,10]

Figure 1 shows a plot of the logarithms of rate constants for solvolyses of *tert*-butyl bromide vs. 1-adamantyl bromide (I, X = Br);[11] the less nucleophilic media, acetic acid, formic acid, 97% trifluoroethanol, and 97% hexafluoropropanol (HFIP), deviate markedly from the correlation line for aqueous ethanol mixtures.



I II III

For these correlations, 1-adamantyl is a good reference substrate because it cannot undergo nucleophilic solvent assistance or elimination.[13] The deviations in Figure 1 are probably associated with mechanistic changes for *tert*-butyl halides which could react either by rate-limiting elimination from a contact ion pair, $k_{-1} > k_2$ in

$$RX \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^+X^- \xrightarrow{k_2} \text{product} \qquad (1)$$

(the currently accepted mechanism),[6,13,17] or by direct nucleophilic attack on covalent substrate, $k_2 > k_{-1}$ (not currently favored but see ref 10b, 18, and 19). These two possibilities can be distinguished by studying a substrate capable of elimination but not susceptible to nucleophilic solvent assistance. 2-Methyl-2-adamantyl chloride (III, X = Cl) is well suited for this purpose because it has been proposed to react by rate-limiting elimination from a contact ion pair,[20,21] and even solvolysis of the secondary 2-adamantyl system is thought to be free from nucleophilic solvent assistance at the α carbon atom[2,3,10b] (a fortiori for III, but solvent-assisted elimination is then possible). There is a good correlation (Figure 2) between solvolyses of *tert*-butyl chloride and III (X = Cl) for aqueous ethanols, with a major deviation for 97% HFIP almost identical

0002-7863/79/1501-2486$01.00/0