

Relative Reactivity of Bridgehead Adamantyl and Homoadamantyl Substrates from Solvolyses with Heptafluorobutyrate as a Highly Reactive Carboxylate Leaving Group. Absence of S_N2 Character of Solvolysis of *tert*-Butyl Derivatives

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Contribution from the Corporate Research-Science Laboratories, Exxon Research and Engineering Company, Clinton Township, Annandale, New Jersey 08801, and Chemisches Laboratorium der Universität Freiburg, 7800 Freiburg, Germany. Received September 4, 1984. Revised Manuscript Received May 6, 1985

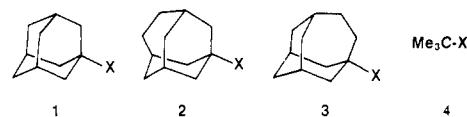
Abstract: Heptafluorobutyrate, conveniently prepared from alcohols, possess a reactivity similar to that of halides in solvolysis reactions. A product and isotope distribution study for the reaction of 1-adamantyl heptafluorobutyrate (**1a**) in 80:20 ethanol-H₂¹⁸O demonstrated exclusive alkyl-oxygen cleavage. The reactivities of **1a**, 1-(**2a**), and 3-homoadamantyl heptafluorobutyrate (**3a**) increase with the flexibility of the hydrocarbon skeleton. The rate constants are linearly correlated with the strain increase upon ionization. No acceleration attributable to nucleophilic solvent assistance was evidenced for the *tert*-butyl ester, **4a**. A literature proposal for such assistance in solvolyses of **4** is examined. The existing data are explained better by an S_N1 process with electrophilic assistance of the leaving group in the solvents that can form very strong hydrogen bonds.

Comparison of rates and products for substrates containing different leaving groups has been extensively used to probe various mechanistic aspects of carbocationic solvolyses, such as intervention of S_N1 or S_N2 mechanisms,² dissociation of tight ion pairs,^{3,4} ion pair return,^{3,4b,5} and, more recently, manifestation of steric interaction in the initial state (reactant) or in the transition state of the reaction.^{6,7} The use of various leaving groups was primarily necessitated, however, by the vast differences which exist between the inherent reactivities of various solvolysis substrates.⁸ In fact, new leaving groups have been introduced for studying new substrates, too reactive or too unreactive for the existing leaving groups.

A problem with the use of different leaving groups for assessing steric interactions in solvolysis^{6,7} is that groups differing in size and shape differ also markedly in nucleofugality.⁹ Thus, the

reactivity of the most common types of leaving groups varies in the following order: substituted benzoates (1) < halides (~10⁴-10⁶) < alkane- and arenesulfonates (~10¹⁰-10¹²) < perfluoroalkanesulfonates (~10¹⁵-10¹⁶).⁸ Therefore, in the study of two reactants differing only by the leaving group, RX₁ and RX₂, rates are normally obtained under very different conditions of solvent and temperature, and comparison involves tenuous extrapolations.^{6b} Also, the rates for at least one of the compounds are often measured under extreme conditions, such as high temperature, so the data have a relatively low accuracy.^{6b,7} These difficulties have been observed in comparisons of solvolysis rates of halides and *p*-nitrobenzoates (carboxylate leaving group) undertaken to assess the steric strain relief upon ionization of bridgehead polycyclic substrates.^{6d,7}

We have found that heptafluorobutyrate (OCOC₃F₇, perfluorobutyrate, OHFB) has a nucleofugality⁹ similar to that of halides,¹⁰ as shown by the solvolysis rates for 1-adamantyl (**1**), 1-homoadamantyl (**2**), 3-homoadamantyl (**3**), and tertiary butyl (**4**) derivatives in Table I.



a. X = OCOC₃F₇ (OHFB); b. X = Cl; c. X = Br; d. X = OCOC₆H₄ NO₂-*p* (OPNB); e. X = OH; f. X = OEt; g. X = I; h. X = H

An advantage of heptafluorobutyrate over halides lies in a more convenient preparation from alcohols, which are the most common intermediates for the synthesis of solvolysis substrates. Moreover, conversion of alcohols to halides is occasionally accompanied by rearrangement, while the esters (ROHFB) are prepared by reactions not breaking the R-O bond.¹¹ Therefore, the heptafluorobutyrate should be the reactant of choice when the study of only one substrate RX is intended.¹²

(10) Preliminary experiments on the solvolysis of 1-OHFB have been conducted at Princeton University, in 1976 (material support and encouragement from Prof. P. v. R. Schleyer are gratefully acknowledged): Fărcasiu, D.; Godleski, S. A., unpublished results.

(11) (a) Perfluorobutyrate has been used for the gas-chromatographic and mass-spectrometric analysis of steroid alcohols and phenols: Clark, S. J.; Wotiz, H. H. *Steroids* **1963**, *2*, 535. See also: Dehennin, L.; Levisalles, J. *Bull. Soc. Chim. Belg.* **1975**, *85*, 333. (b) The use of HFB esters for alcohol derivatization in NMR studies with lanthanide shift reagents has been reported: Cockerill, A. F.; Davies, G. L. O.; Harden, R. C.; Rackham, D. M. *Chem. Rev.* **1973**, *73*, 553, especially p 578.

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(8) For collections of solvolysis rates for substrates with various leaving groups, see: (a) Hughes, E. D. *J. Chem. Soc.* **1935**, 255. (b) Bateman, L. C.; Cooper, K. A.; Hughes, E. D.; Ingold, C. K. *J. Chem. Soc.* **1940**, 925. (c) Fainberg, A. M.; Winstein, S. *J. Am. Chem. Soc.* **1957**, *79*, 1602. (d) Schleyer, P. v. R.; Nicholas, R. D. *J. Am. Chem. Soc.* **1961**, *83*, 2700. (e) Stetter, H.; Goebel, P. *Chem. Ber.* **1963**, *96*, 550. (f) Stepanov, F. N.; Guts, S. S. *Zh. Org. Khim.* **1968**, *4*, 1933. (g) Brown, H. C.; Dickason, W. C. *J. Am. Chem. Soc.* **1969**, *91*, 1226. (h) Raber, D. J.; Bingham, R. C.; Harris, J. M.; Fry, J. L.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 5977. (i) References 6b, 6c. (j) Crossland, R. K.; Wells, W. E.; Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 4217. (k) Su, T. M.; Sliwinski, W. S.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1969**, *91*, 536; Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85.

(9) Nucleofugality represents the ability of an atom or group of atoms (nucleofuge) to separate from a molecule with both electrons that had formally bonded it to the rest of the molecule. See: Stirling, C. J. M. *Acc. Chem. Res.* **1979**, *12*, 198.

Table I First-Order Rate Constants for Solvolyses^a

compound	temp., °C	<i>k</i> , s ⁻¹	Δ <i>H</i> [‡] , ^b kcal/mol	Δ <i>S</i> [‡] , ^b eu	<i>k</i> _{rel}				
1-adamantyl-OHFB ^{c,d}	25.0	1.50 × 10 ^{-8 e}	25.6 ± 0.1 ^f	-8.6 ± 0.3 ^f	1				
	50.0	4.59 × 10 ^{-7 e}							
	75.0	1.13 × 10 ^{-5 g}							
	80.1	1.10 × 10 ⁻⁵							
	89.8	3.65 × 10 ⁻⁵							
	100.0	1.19 × 10 ^{-4 g}							
	100.6	1.28 × 10 ⁻⁴							
	120.1	6.35 × 10 ⁻⁴							
	127.2	1.27 × 10 ⁻³							
	1-adamantyl-Cl ^h	25.0				7.64 × 10 ⁻⁹	25.5	-10.2	0.5
	1-adamantyl-Br ⁱ	25.0				2.29 × 10 ⁻⁷	22.4	-12.3	34
50.0		1.03 × 10 ⁻⁵							
1-homoadamantyl-OHFB ^{c,j}	25.0	7.73 × 10 ^{-8 e}	24.7 ± 0.04 ^k	-8.2 ± 0.1 ^k					
	50.0	2.12 × 10 ^{-6 e}							
	64.9	1.12 × 10 ⁻⁵							
	75.1	4.00 × 10 ⁻⁵							
	89.9	1.72 × 10 ⁻⁴							
	102.9	5.25 × 10 ⁻⁴							
	108.1	8.78 × 10 ⁻⁴							
3-homoadamantyl-OHFB ^{c,j}	25.0	2.92 × 10 ^{-6 e}	21.9 ± 0.03 ^l	-10.3 ± 0.1 ^l					
	49.7	5.15 × 10 ⁻⁵							
	50.0	5.54 × 10 ^{-5 e}							
	59.6	1.63 × 10 ⁻⁴							
	69.8	4.23 × 10 ⁻⁴							
	80.1	1.05 × 10 ⁻³							
	84.9	1.76 × 10 ⁻³							
	<i>t</i> -Bu-OHFB ^c	25.0				3.97 × 10 ^{-6 e}	20.9 ± 0.3 ^m	-13.0 ± 0.1 ^m	265 (1)
	49.7	6.34 × 10 ⁻⁵							
	50.0	6.62 × 10 ^{-5 e}							
59.4	1.71 × 10 ⁻⁴								
75.2	7.68 × 10 ⁻⁴								
80.2	1.28 × 10 ⁻³								
84.2	1.49 × 10 ⁻³								
<i>t</i> -Bu-Cl ⁿ	25.0	9.14 × 10 ⁻⁶	22.4	-6.4	609 (2.3)				
	50.0	1.85 × 10 ⁻⁴							
<i>t</i> -Bu-Br ^o	25.0	3.58 × 10 ⁻⁴	21.5	-2.3	23 900 (90)				
	50.0	6.40 × 10 ⁻³							

^aIn ethanol-water (80:20 (v/v), ref 8b). ^bCalculated with the program in ref 44a. ^cThis work. ^dReported rates for OPNB esters (3.05 × 10⁻¹⁰, 80% AcMe, 70 °C, ref 6d; 3.68 × 10⁻⁵, 70% acetonitrile, 150 °C, ref 7b) have only orientative value. ^eCalculated from data at other temperatures. ^fThe program in ref 44b gives 25.4 ± 0.8, -9.0 ± 2.1. ^gReference 10. ^hRecalculated from data in ref 8d. ⁱReference 8h. ^jFor rates of halides see ref 16. ^kThe program in ref 44b gives 25.1 ± 0.7, -7.0 ± 1.9. ^lThe program in ref 44b gives 22.4 ± 0.7, -8.8 ± 2.1. ^mThe program in ref 44b gives 21.3 ± 0.14, -12.0 ± 0.4. ⁿReference 8a, see also: ref 32. ^oReference 8c, see also ref 8b.

Product and Isotope Distribution Studies. In the solvolyses of **1a-3a** in 80% ethanol,^{8b} the corresponding alcohols (**1e-3e**) and ethyl ethers (**1f-3f**) were formed in 94-96% combined yield. Moreover, the alcohol **1e** obtained from **1a** in ethanol-H₂¹⁸O at 110 °C was labeled to the same extent as the solvent. Therefore, the heptafluorobutyrate reacted by an S_N1 process, without any acyl-oxygen cleavage.

The product distribution from **1a-3a** was essentially the same (64:36 alcohol, **1e-3e**, to ether, **1f-3f**) and reasonably close to the distribution reported from 1-adamantyl bromide (**1c**) (60:40 and 49:51 **1e:1f** at 60 and 75 °C, respectively)¹³ and from the corresponding tosylate (71:29 **1e:1f** at 25 °C).¹⁴ The product mixture from **4a** (20% **4e**, 40.5% **4f**, and 39.5% olefin) was significantly richer in ether than the product mixture from **4c** (57.1% **4e**, 28.4% **4f**, and 14.5% olefin).¹⁵ No significant change in product composition with temperature was observed for **1a** (80-127 °C), **2a** (75-108 °C), and **4a** (59-84 °C).

Reactivity of Bridgehead Homoadamantyl Substrates in Solvolysis. Little reliable information is available on the solvolysis

of isomeric bridgehead homoadamantyl substrates (**2**, **3**). The early kinetic data^{8c,f} were obtained on materials that were not adequately characterized.^{7a,16} Newer attempts to prepare pure bromides **2c** and **3c** have encountered major difficulties.^{7,17} On the other hand, solvolysis of the *p*-nitrobenzoates (**2d**, **3d**) prepared from the corresponding alcohols could be conducted only under special conditions of temperature and solvent, thus making comparison with other polycyclic systems difficult.⁷ Use of the OHFB leaving group eliminates these problems and allows a direct comparison of **2** and **3** with other substrates, such as 1-adamantyl and *tert*-butyl (**4**). As expected based on literature,^{6,18} the reactivity in solvolysis increases with the flexibility of the carbon skeleton. In fact, the rates for perfluorobutyrate **1a-4a** (Table I) obey a linear relationship with the calculated strain increase upon ionization (eq 1, *a* = 0.54, *b* = 11.9, correlation coefficient *r* = 0.992, in 80% ethanol at 25 °C), of the kind described by Bingham and Schleyer.^{6a,b,19}

$$-\ln k = a\Delta(\text{strain}) + b \quad (1)$$

(12) The lower homologue, trifluoroacetate, can be estimated to be about 100 times less reactive than the heptafluorobutyrate: Winter, J. G.; Scott, J. M. W. *Can. J. Chem.* **1968**, *46*, 2886. Alberly, W. J.; Robinson, B. H. *Trans. Faraday Soc.* **1969**, *65*, 890. Winter, J. G.; Scott, J. M. W. *Can. J. Chem.* **1972**, *50*, 1886.

(13) (a) MacMillan, J.; Pryce R. J. *J. Chem. Soc. B*, **1970**, 337. (b) Harris J. M.; Raber, D. J.; Hall, R. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 5729.

(14) Kevill, D. N.; Kolwyck, K. C.; Weilt, F. L. *J. Am. Chem. Soc.* **1970**, *92*, 7300.

(15) Cocivera, M. Ph.D. Thesis, UCLA, 1963, quoted in ref 14.

(16) The structures of materials solvolyzed (in 80% ethanol) as **2c** (*k* = 5.75 × 10⁻⁵ s⁻¹, at 50 °C, ref 8f), **3b** (*k* = 6.62 × 10⁻⁵ s⁻¹ at 50 °C, ref 8e), and **3c** (*k* = 2.23 × 10⁻³ s⁻¹ at 50 °C, ref 6b, 8e) were in fact unknown. See ref 7, 17.

(17) (a) Goltzke, V. Ph.D. Thesis, University of Freiburg, 1976. (b) Langhals, H.; Rüdhardt, C. *Chem. Ber.* **1974**, *107*, 1245. (c) Langhals, H.; Mergelsberg, I.; Rüdhardt, C.; Bürger, U. *Chem. Ber.* **1982**, *115*, 1509. (d) Godleski, E. A.; Graham, W. D.; Bentley, T. W.; Schleyer, P. v. R.; Liang, G. *Chem. Ber.* **1974**, *107*, 1257. (e) See also: Israel, R. J.; Murray, R. K. *J. Org. Chem.* **1983**, *48*, 4701.

(18) Gleicher, G. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1967**, *89*, 582.

In eq 1 $\Delta(\text{strain})$ is the difference between the strain energies for the carbocation (R^+) and the corresponding hydrocarbon (RH),^{6b} obtained by molecular mechanics calculations. The strain energy values employed in previous correlations^{6a,b,19b,c} have been the "raw" steric energies,²⁰ obtained as the sum of bond stretching, angle bonding, twisting, and nonbonded interaction strain, with the force field for carbocations and hydrocarbons of Bingham and Schleyer.^{6a-c} For better comparison with the earlier work we have used here the same approach.²¹ The $\Delta(\text{strain})$ values were 11.9, 7.5, 1.6, and 1.4 kcal/mol for **1**, **2**, **3**, and **4**, respectively.²²

Test for S_N2 Character of Solvolysis of *tert*-Butyl Substrates. Some interesting observations can be made from the comparison of solvolysis rates for the heptafluorobutyrate of the bridgehead alcohols (**1a**–**3a**) and for *t*-Bu-OHFB (**4a**).

It has been reported that the rate ratio of *tert*-butyl bromide (**4c**) to 1-adamantyl bromide (**1c**) varies from one thousand or more in ethanol to 2.5 in 97% hexafluoroisopropyl alcohol (HF-IP).²³ This variation was explained by intervention of nucleophilic solvent assistance for **4c** in ethanol. In a more extensive study²⁴ the empirical eq 2, relating the rate constants in a given solvent (k) and the rate constants in 80% ethanol (k_0), held for most solvent mixtures, but the rates for **4** in carboxylic acids and fluorinated alcohols as solvents showed deviations from the line (were too slow). The deviations were taken to mean a reduction in nucleophilic assistance in these solvents.^{23,24}

$$\log(k/k_0)_4 = C \log(k/k_0)_1 \quad (2)$$

If the rate ratio in HFIP represents the ratio of unimolecular rate constants (k_c) of **4** and **1**,²³ then the change in k_4/k_1 from HFIP to other solvents should measure the nucleophilic solvent assistance operating in the solvolysis of **4**.^{23,25} Thus for bromides in 80% ethanol at 25 °C ($k_{4c}/k_{1c} = 700$)²³ this assistance would represent a rate factor of 280 (700/2.5); for heptafluorobutyrate ($k_{4a}/K_{1a} = 265$, Table I) it would be a factor of 106 (265/2.5) and for chlorides ($k_{4b}/k_{1b} = 630$)²⁴ a factor of 250. These numbers could well be only minimum values, since it has been noted that solvolysis of **4** may be not limiting in 97% HFIP.²³ Indeed, in the latter solvent the relative rates for solvolysis of *tert*-butyl and 2-propyl bromides (α -methyl effect)²⁶ are $10^{6.2}:1$, rather than $10^{7.5-10^8}:1$ (limiting value).^{23,27} As one of us has shown before, the viewpoint that the limiting α -methyl effect should be the same in all systems is not correct.²⁶ Nevertheless, there is enough uncertainty in previous work^{23,24} to preclude a quantitative

evaluation of nucleophilic solvent participation in the solvolysis of **4**.

Equation 1, however, provides in principle the means to make this evaluation since the bridgehead substrates (**1**–**3**) cannot use nucleophilic assistance in any solvent. The deviation of **4** (too fast) from the line defined by eq 1 should represent the nucleophilic solvent assistance.

As it turned out, instead of being too fast by a factor of at least 106, the rate of **4a** in 80% ethanol was well correlated by eq 1 together with the rates for **1a**–**3a** (see above). The solvolysis of the *tert*-butyl substrate **4a** is thus not nucleophilically assisted.

We realized, however, that this conclusion had to be treated cautiously. After all, ours was a somewhat limited reaction series, covering four substrates and a reactivity span of only 260. Therefore, we tested the reliability of the predictions of eq 1 in two ways. First, we correlated the heptafluorobutyrate solvolysis rate constants with strain energies calculated with a different force field, namely that of Engler, Andose, and Schleyer.^{20,22a} The steric energy numbers obtained with two force fields are normally different, since "each parameter set represents a different blend of strain components".²⁰ While the absolute numbers cannot be compared directly, arriving at the same qualitative prediction with two different force fields increases the credibility of the prediction.^{19c,20}

As expected, introduction of steric energies calculated with the other force field^{20,22a} (21.6, 13.6, 4.5, and 0.2 kcal/mol for **1**, **2**, **3**, and **4**, respectively) in eq 1 led to different values for slope and intercept ($a = 0.28$, $b = 12.1$, correlation coefficient $r = 0.985$) than noted above. There was no upward deviation, however, for the point for the *tert*-butyl derivative (**4a**) from this line, either.

Secondly, we examined the application of eq 1 to the solvolysis of chlorides, including **4b**. Bingham and Schleyer have reported this correlation for nine substrates;^{6b} we have added 1-*cis*-bicyclo[4.4.0]decyl chloride²⁸ to their list. Our reaction series thus consisted of ten bridgehead chlorides²⁹ and **4b**, and covered a reactivity span of more than six powers of ten in 80% ethanol at 70 °C.^{6b,28} Again, the point for **4b** did not deviate from the line ($a = 0.67$, $b = 5.92$, $r = 0.960$) obtained with the strain energies calculated with the Bingham–Schleyer force field.²⁹ Excluding **4b** from the correlation did not alter the line to any significant extent ($a = 0.67$, $b = 5.99$, $r = 0.958$).³⁰ Thus, the strain-reactivity correlation does not reveal any nucleophilic assistance for chloride **4b** either. As the figures shown above indicate, the mechanistic model of Bentley et al.^{23,24} requires an even higher deviation from eq 1 for the chloride **4b** than for the heptafluorobutyrate **4a**.

Trying to understand the reasons for the discrepancy between our findings and the conclusions of Bentley et al.,^{23,24} we reexamined the treatment of data in the earlier papers.^{23,24} This reexamination is detailed in the Appendix. It appears from it that nucleophilic solvent assistance is not needed to explain the different responses of 1-adamantyl (**1**) and *tert*-butyl (**4**) substrates to the change of solvent from aqueous alcohols and the like to HFIP, TFA, and the like. On the contrary, the model involving the nucleophilic assistance for **4** leads to the wrong predictions for the rate response to solvent changes (see Appendix).

Alternative explanations for the seemingly peculiar behavior of the fluorinated alcohols and acid solvents have been proposed before.^{8h,31} Additionally, the rate effects observed^{23,24} could result

(19) (a) For other examples of application of eq 1 see: Fărcașiu, D. *J. Org. Chem.*, **1978**, *43*, 3873 and references therein. (b) See also: Ōsawa, E.; Engler, E. M.; Godleski, S. A.; Inamoto, Y.; Kent, G. J.; Kausch, M.; Schleyer, P. v. R. *J. Org. Chem.* **1980**, *45*, 984. (c) Parker, W.; Tranter, R. L.; Watt, C. I. F.; Chang, L. W. K.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 7121.

(20) Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005.

(21) (a) In our other work^{19a} we have used the $\Delta H(\text{strain})$ values, obtained by comparing the calculated heats of formation with the values obtained from "strainless" increments.²⁰ We have tested in the present study correlations with $\Delta H(\text{strain})$ as well. The conclusions were exactly the same, only the values of a and b in eq 1 were slightly different. (b) Correlations with $\Delta H(\text{strain})$ rather than steric energy have been reported also by Smith, P. R.; Harris, J. M. *J. Org. Chem.* **1978**, *43*, 3588.

(22) (a) The computer program used was BIGSTRN2 (Iverson, D. J.; Mislow, K. *QCPE* **1980**, No. 410) which is an expanded version on BIGSTRN (Andose, J. D.; Engler, E. M.; Collins, J. B.; Hummel, J. P.; Mislow, K.; Schleyer, P. v. R. *QCPE* **1977**, No. 348). (b) BIGSTRN2 gives a better minimization in the calculation of steric energies with the Bingham force field (ref 6a) than the original program of ref 6c. (c) The incorporation of the Bingham force field into the BIGSTRN2 program will be discussed elsewhere.

(23) Bentley, T. W.; Bowen, C. T.; Parker, W.; Watt, C. I. F. *J. Am. Chem. Soc.* **1979**, *101*, 2486.

(24) Bentley, T. W.; Carter, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 5741.

(25) A reviewer of the manuscript has observed that the treatment in ref 23 is based on the assumption of nucleophilic assistance occurring only from the back, and that this assumption might not be correct. While the idea of front-side solvation of the carbocation in the rate-determining step might have merits, this mechanistic problem is beyond the scope of the present article.

(26) Fărcașiu, D. *J. Am. Chem. Soc.* **1976**, *98*, 5301.

(27) Fry, J. L.; Harris, J. M.; Bingham, R. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 2540.

(28) The solvolysis rate constant for this compound was reported by Boschung, A. F.; Geisel, M.; Grob, C. A. *Tetrahedron Lett.* **1968**, 5169.

(29) Our correlation included the following substrates (with the strain energy differences calculated with the Bingham–Schleyer force field^{6,22b} in parentheses): 1-bicyclo[3.3.2]decyl (–1.2), **3** (1.6), 1-*cis*-bicyclo[4.4.0]decyl (2.6), 1-*trans*-bicyclo[4.4.0]decyl (3.1), 1-*trans,trans,trans*-tricyclo[7.3.1.0^{5,13}]tridecyl (3.3), 13-*cis,cis,trans*-tricyclo[7.3.0^{5,13}]tridecyl (4.3), 1-bicyclo[3.2.2]nonyl (5.1), 1-bicyclo[3.3.1]nonyl (6.6), **1** (11.9), and 1-tricyclo[4.4.0.0^{4,9}]decyl (20.0).

(30) (a) Correlation with strain energy differences calculated with the force field of ref 20 also shows no deviation for **4b**. (b) The strain-reactivity correlation applied for bromides shows no deviation for the *tert*-butyl substrate, **4c**, either.

(31) Shiner, V. J., Jr.; Dowd, W.; Fisher, R. D.; Hartshorn, S. R.; Kessic, M. A.; Milakofsky, L.; Rapp, M. W. *J. Am. Chem. Soc.* **1969**, *91*, 4838.

from electrophilic assistance of leaving group departure by these solvents.

The electrophilic assistance of the leaving group has been recognized in the original studies of the medium effects in solvolysis reactions,^{32,33a,f} as well as in more recent work,³⁴ together with solvent polarity and nucleophilicity. As a first approximation, electrophilicity was incorporated into the empirical solvent polarity parameter.^{24,32a,35} What resulted was the well-known two-term Winstein–Grunwald equation (eq 3 in the Appendix).³² More recently, it was reported that the rates of ionization of *tert*-butyl halides (**4b**, **4c**, and the corresponding iodide) are dependent on solvent polarity and solvent electrophilicity but not on solvent nucleophilicity.³⁶ The cage structure compounds such as **1** and 2-methyl-2-adamantyl chloride²³ seem to have a higher sensitivity than **4** to electrophilic assistance to the atom or group separating as an anion. Indeed, electrophilic assistance by metal ions ($\text{Co}^{2+} > \text{Li}^+ > \text{Na}^+$) to ionization in acetonitrile is important for adamantyl substrates, but small for *tert*-butyl substrates,³⁷ while electrophilic assistance of *tert*-alkyl iodide solvolyses by iodine is significantly more pronounced for **1g** than for **4g**.³⁸ Moreover, in the latter case the iodine assistance is much more pronounced in ethanol than in HFIP as solvent,³⁸ undoubtedly because the electrophilicity of HFIP itself levels off the iodine effect. As another example, hydride transfer (electrophilic attack at hydrogen) from the corresponding hydrocarbons is significantly faster for **1h** than for **4h**.³⁹ In the light of these data, the deviations observed from eq 2 in nonnucleophilic (electrophilic) solvents^{23,24} are due to **1** being too fast, rather than **4** being too slow.

In summary, it appears to us that for the solvolysis of *tert*-butyl substrates, the kinetic consequences of nucleophilic solvent assistance (if any) in aqueous ethanol and similar solvents are unimportant in comparison to the kinetic consequences of electrophilic solvent assistance in TFA, HFIP, and similar solvents. It might, perhaps, be expected that heptafluorobutyrate would benefit less from electrophilic assistance than halides or sulfonates. In any event, since the range of solvents in use today is much wider than those on which the original Winstein–Grunwald treatment was based,³² a three-term correlation including solvent polarity, electrophilicity, and nucleophilicity,³⁶ should be preferred in principle over a two-term correlation such as eq 3.^{33,40}

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Experimental Section

1-Homoadamantyl Methyl Ketone (5),^{17b,c,41} A 1.7 M methylolithium solution (70 mL, 119 mmol) was added dropwise to a stirred, ice-chilled solution of 1-homoadamantanecarboxylic acid (8.7 g, 45 mmol) in anhydrous ether (300 mL) under nitrogen. The solution was boiled under reflux for 2 h, cooled in ice again, treated with 1 mL of dry acetone, and decomposed with water. The resulting mixture was extracted with ether, the ether phase was dried (MgSO_4), and the solvent was distilled off. The product (6.3 g, 73.5% yield) boiled at 81.5–83 °C (0.04 mm Hg) (lit.⁴¹ bp 95 °C (0.05 mm Hg)).

1-Homoadamantanol (2e). (a) **From Ketone 5**,^{17b,c,41} Trifluoroacetic anhydride (6 mL, 43 mmol) was added dropwise to 85% H_2O_2 (1.0 mL)⁴² dissolved in dry methylene chloride (40 mL), at 0 °C. The solution was then added to a mixture of **5** (3.2 g, 16.6 mmol) dissolved in dichloromethane and disodium hydrogen phosphate (20 g, 140 mmol, dried over phosphorus pentoxide). The reaction was slightly exothermic. The solution was boiled under reflux for 2.5 h when the ketone was all reacted (GLC on a 1 m, 1% silicone SE-30 column at 160 °C). The solution was filtered and washed with sodium bicarbonate solution and with water, and then the acetate (**2**, X = OCOCH_3) was hydrolyzed with methanol (50 mL), potassium hydroxide (10 g), and water (5 mL) for 7 h under reflux. Standard workup and crystallization from light petroleum (bp 90–100 °C) afforded 0.8 g (29%) of **2e**, mp 255 °C (lit.⁴¹ mp 267.5–268.5 °C). The IR spectrum was identical with that of an authentic material.^{7b} GLC (25 m glass capillary column, Carbowax-20M at 120 °C) showed the material to consist of 96% **2e** and 4% **3e**.

(b) **From 1-Homoadamantylamine (6)**,^{7b,17c} The amine **6** (2.85 g, 17.3 mmol) dissolved in acetic acid (2 mL) and water (16 mL) was treated with a solution of sodium nitrite (1.6 g, 23.1 mmol) in water (5 mL), added over a period of 30 min. The solution was then heated for 1 h at 90 °C. The crystals which precipitated were filtered, washed with water, dried, and crystallized from light petroleum (bp 90–100 °C), giving 0.8 g (28%) of **2e** identified by IR (see above).^{7b} GLC (as above) showed 89.5% **2e** and 10.5% **3e**.

1-Adamantanecarboxamide (7),⁴¹ 1-Adamantanecarboxylic acid (37.0 g, 205 mmol) was boiled for 2 h under reflux in an inert atmosphere with thionyl chloride (50 mL) and dimethylformamide (1 drop). The thionyl chloride excess was distilled off under vacuum, then the traces were removed with an oil vacuum pump for 30 min. The residue was dissolved in tetrahydrofuran (THF) (100 mL) and added to 500 mL of concentrated aqueous ammonia, with ice cooling and stirring. After stirring for 1 h at room temperature, the amide was filtered off, dried, and recrystallized from cyclohexane–methylene chloride (1:1). Yield: 29.3 g (74%), mp 185 °C (lit.⁴¹ mp 187 °C).

1-Adamantylmethylamine (8),^{17b,41} The amide **7** (29 g, 162 mmol) dissolved in anhydrous THF (400 mL) was added dropwise under nitrogen to a suspension of lithium aluminum hydride (17.5 g, 449 mmol) in boiling THF (500 mL, anhydrous). The mixture was boiled under reflux for 3 days, then it was hydrolyzed with water and 2 N NaOH. The precipitate of aluminum hydroxide was extracted several times with boiling THF, the combined organic solution was dried (MgSO_4), the solvent was evaporated, and the residue was distilled under vacuum. The yield of **8** was 21 g (78%), bp 72–75 °C (0.05 mmHg).

3-Homoadamantanol (3e),^{7b,17b,41} To a solution of **8** (20.0 g, 121 mmol) in acetic acid (14 mL) and water (110 mL), sodium nitrite (11.0 g, 159 mmol) dissolved in water (30 mL) was added over a period of 1 h. The mixture was then heated for 1.5 h at 90 °C, and the solid was filtered off, washed with water, dried, and recrystallized from light petroleum (bp 90–100 °C) to yield 14.2 g (71%) of **3e**. The melting point (244 °C, with sublimation) was lower than found by previous workers (mp 266 °C,^{7b} 273–4 °C⁴¹). Admixture of material from the former source^{7b} into our sample did not alter the melting point; the two materials had identical IR spectra. GLC analysis (as for **2e**) gave a purity of over 99% **3e**; no **2e** was evidenced.

Preparation of Heptafluorobutyrate (1a–4a). To alcohol (20 mmol) dissolved in 10 mL of anhydrous pyridine, heptafluorobutyryl chloride (7.8 g, 33.3 mmol) dissolved in dry dichloromethane (20 mL) was added dropwise with stirring, cooling, and exclusion of moisture. The mixture was stirred for 12 h at 0 °C, and then treated with ice–water and methylene chloride. The organic phase was washed with diluted hydrochloric acid, sodium bicarbonate, and water, making sure that the temperature stayed below 5 °C. The solution was dried (MgSO_4), the solvent was distilled off, and the residue was purified by column chromatography on silica gel in petroleum ether. The purity of the product was checked by TLC (one spot). The esters **1a–4a** were all liquids and were obtained

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(42) This material was analyzed by titration with $\text{KI}/\text{Na}_2\text{S}_2\text{O}_3$ (Vogel, A. I. In "Textbook of Quantitative Inorganic Analysis", 4th ed.; Longman: London, 1978). No reaction took place with 54% H_2O_2 .

in yields of 74% (**1a**), 70% (**2a**), 74% (**3a**), and 60% (**4a**). IR $\nu_{\text{C=O}}$ at 1768 (**1a**), 1765 (**2a**), 1770 (**3a**), and 1775 cm^{-1} (**4a**). Satisfactory elemental analyses (C, H) were obtained for **1a–3a**, but **4a** contained small amounts of solvent (GLC, 25 m capillary column, silicone SE-30, 50 °C, injector at 80 °C, retention time of **4a** 6.5 min). Due to its high volatility (bp 60 ± 5 °C at 760 mm) **4a** was purified by bulb to bulb distillation in an evacuated sealed installation below 0 °C, rather than by column chromatography. MS, (70 eV) m/e (relative intensity): (**1a**) 348 (M^+ , less than 1%), 135 (100), 134 (82), 93 (20), 92 (76), 91 (27), 79 (38), 78 (23), 77 (22), 69 (23), 68 (22), 56 (22), 41 (41), 40 (14), 39 (29); (**4a**) 255 ($M - \text{CH}_3$, 38), 254 (8), 169 (29), 168 (5), 100 (6), 69 (43), 61 (10), 57 (100), 56 (18), 55 (8).

Rate Measurements. For temperatures below 60 °C, $2-3 \times 10^{-3}$ M solutions of the substrates were prepared in a conductimetric cell^{7b} and equilibrated at the temperature indicated (Table I) before taking the first reading. The infinity point was taken after 10 half-lives. The earlier measurements at temperatures over 60 °C were made in the same way as above,¹⁰ while the ampule technique was used for the newer determinations.⁴³ For these measurements, $4-6 \times 10^{-2}$ M solutions of the substrates were prepared and 1.5 mL of solution were sealed in each ampule. The ampules (13–16 per experiment) were thermostated at the indicated temperature (Table I). For analysis an ampule was chilled and cut open, 1 mL of solution was removed with a pipet and diluted with exactly 25 mL of the alcohol–water mixture, and the conductivity of the resulting solution was measured. The initial point was taken after 5 min and the infinity point after 10 half-lives. The first-order rate constants were obtained by least-square fitting of conductivity data.⁴⁴

Product analysis was conducted by GLC (2 m, 15% silicone-SE 30 at 165 °C for **1a–3a** and at 5 °C for **4a**) with diethyl phthalate (for **1a–3a**) and 2-methyl-2-butanol (for **4a**) as integration standards. The products were identified by retention time comparison with authentic samples and by GLC-MS.

Labeling Experiment. A solution of **1a** (18.9 mg, 5.43×10^{-2} mmol) in 635.9 mg (0.8101 mL) of ethanol and 249.7 mg (0.2365 mL) of H_2^{18}O ($55 \pm 3\%$ ^{18}O by MS) was sealed in an ampule and heated at 110 °C for 5 h, and then opened and analyzed by GC-MS (70 eV, see above). **1f**: 181 (6), 180 (34), 135 (12), 124 (11), 123 (84), 122 (12), 96 (6), 95 (51), 94 (16), 93 (12), 91 (8), 87 (7), 81 (7), 79 (19), 77 (11), 69 (6), 67 (13), 58 (5), 55 (14), 53 (7), 44 (100), 43 (20), 42 (7), 41 (28). **1e** (standard): 152 (18), 96 (10), 95 (100), 94 (27), 79 (8), 77 (9), 67 (7), 55 (8), 44 (31), 43 (10), 41 (16). **1e** (labeled): 154 (20), 153 (6), 152 (14), 98 (11), 97 (100), 96 (28), 95 (72), 94 (25), 93 (5), 91 (5), 79 (14), 77 (15), 67 (12), 55 (10), 53 (8), 45 (5). Thus, **1e** contains 60% ^{18}O while **1f** is unlabeled.

Appendix

A. In order to rationalize the deviations observed from eq 2 established as a purely empirical relationship,²⁴ we have to determine first what physical meaning, if any, eq 2 has. If we assume that solvolysis of **4** is, indeed, nucleophilically assisted, the solvent effects upon the rates of **4** and **1** can be described by the appropriate forms of the Winstein–Grunwald relationship, eq 3 and 4, respectively.^{32,33,40} (These equations were accepted as valid by Bentley and Carter.^{24,45})

$$\log(k/k_0)_4 = m_4 Y + l_4 N \quad (3)$$

$$\log(k/k_0)_1 = m_1 Y \quad (4)$$

The meaning of parameters m (substrate sensitivity to solvent ionizing power), Y (solvent ionizing power), l (substrate sensitivity to solvent nucleophilicity), and N (solvent nucleophilicity) has been amply discussed before.^{32,33}

Equation 3 divided by eq 4 gives

$$[\log(k/k_0)_4]/[\log(k/k_0)_1] = m_4/m_1 + l_4 N/Y m_1 \quad (5.0)$$

or

$$\log(k/k_0)_4 = (1/m_1)(m_4 + l_4 N/Y) \log(k/k_0)_1 \quad (5.1)$$

Equation 5.1 elucidates the physical meaning of eq 2, since it shows that in the latter

$$C = (1/m_1)(m_4 + l_4 N/Y) \quad (6)$$

Therefore, in eq 2, C is a constant: (a) for any solvent if $l_4 = 0$ (then $C = m_4/m_1$); (b) for a group of solvents for which, fortuitously, N/Y is a constant even though $l_4 \neq 0$.⁴⁶

The physical model assumed by the previous authors^{23,24} requires that $(N/Y) = \alpha$ (constant), since the alternative $l_4 = 0$ was rejected by the authors. The magnitude of $(l_4 \alpha)$ has no importance, as long as it is not identical with zero:

$$\log(k/k_0)_4 = (1/m_1)(m_4 + l_4 \alpha) \log(k/k_0)_1 \quad (5.2)$$

To comply with the same model, the solvents that deviated from the line described by eq 2 (identical with 5.2) must obey eq 5.1 with $N/Y \neq \alpha$. In this case, the deviation of the points for those solvents (acids and fluorinated alcohols) must be described by eq 7, which is the difference between eqs 5.1 and 5.2:

$$\delta = [\log(k/k_0)_4]_{\text{meas}} - [\log(k/k_0)_4]_{\text{calcd}} = (l_4/m_1)(N/Y - \alpha) \log(k/k_0)_1 \quad (7.0)$$

Substitution of numerical values for N , Y ,⁴⁷ and rate constants^{23,24} should allow us to calculate the deviations observed from the line arrived at empirically (eq 2),²⁴ if the model assumed there ($l_4 \neq 0$)^{23,24} is correct. The quantity α is calculated from the N and Y parameters of the well-behaved solvents⁴⁸ (on or near the straight line in the plot).²⁴ For the solvolysis of chlorides, eq 7.0 then becomes

$$\delta = l_{4b}(N/Y + 0.073) \log(k/k_0)_{1b} \quad (7.1)$$

It is then predicted by eq 7.1, with the appropriate N and Y values,⁴⁷ that the magnitude of the deviation from the line should vary in the order 70% AcMe ($0.47l_{4b}$) < 50% TFE ($0.80l_{4b}$) < 70% TFE ($1.07l_{4b}$) < HCOOH ($1.94l_{4b}$) < AcOH ($2.29l_{4b}$) < 97% TFE ($2.69l_{4b}$) < 97% HFIP ($4.00l_{4b}$) < TFA ($4.93l_{4b}$). In particular, a large difference is predicted between 70% TFE and HCOOH, while acetic acid should deviate almost as much as 97% trifluoroethanol. These predictions are in contradiction with the experimental findings (acetic acid²³ and formic acid^{23,24} show small deviations while 70% TFE deviates significantly, and 97% TFE almost twice as much as 70% TFE).²⁴ Thus, the assumption of nucleophilic solvent assistance ($l_{4b} \neq 0$) leads to wrong predictions for the rates of **4b**.

B. As an alternative verification we observed that solvolysis rates of **4b** were correlated with the four-parameter eq 3;²⁴ use of the solvent nucleophilicity parameters of Kevill and Lin ($N_{K,L}$)^{33e,49} gave a sizable value of 0.37 for l_{4b} .^{24,50} We found, however, that when the $l_{4b}N_{K,L}$ term is dropped the correlation for nucleophilic solvents is not affected (the standard deviation remains the same) *even if the value of m is not re-optimized*.⁵¹ It is the group of nonnucleophilic solvents (acids and fluorinated

(46) The possibility $N = 0$ (solvents with the same nucleophilicity as 80% ethanol) represents a particular case of (b).

(47) Of the various sets of Y in existence, we chose the $Y_{1-\text{ADCl}}$ parameters of ref 24, whence $m_1 = 1$ (use of $Y_{2-\text{ADOTs}}$ from ref 33a does not alter the conclusions). To obtain nucleophilicity parameters, N , similar to those of ref 33a,b, the eq $N = \log(k/k_0)_{\text{MeOTs}} - 0.233Y_{1-\text{ADCl}}$ has to be used (this equation was established after an exchange of letters with T. W. Bentley).

(48) (a) Of the 21 solvent mixtures for which the chloride rate constants were found in ref 24 to obey eq 2, rate constants for methyl tosylate are available for 8 (water, 70, 60, 50% ethanol, 70, 60, 50% methanol, 50% acetone), so N can be calculated (ref 47). The first seven gave an average N/Y value (α in eq 5.2 and 7.0) of -0.073 . For all eight solvents $N/Y = -0.094$ but the value for 50% acetone (AcMe) deviates by more than two standard deviations from the average. (b) Five more solvents (100, 90% ethanol, 100, 90, 80% methanol) could in principle be added to the list. The rates for this second group of solvents were not measured, however, but calculated in ref 24 by application of eq 2. Therefore, they cannot be used to test the same equation.

(49) The underlying assumptions for the calculation of $N_{K,L}$ seem sounder than those for the calculation of N from ref 33a,b (see the discussion in ref 33e). We do not wish to debate here that issue, however. We used $N_{K,L}$ parameters simply because the authors in ref 24 had used them. (Actually, ref 24 notes that the choice of N values is not critical to the argument presented there.)

(50) For comparison, solvolysis rates for isopropyl tosylate were correlated in ref 33e with $l = 0.50$.

(51) The correlations $\log(k)_{4b}$ vs. $\log(k)_{1b}$ and $\log(k)_{4b}$ vs. Y are physically one and the same, since Y is defined by $\log(k)_{1b}$.

(43) Jähme, J. Ph.D. Thesis, University of Freiburg, 1983.

(44) (a) DeTar, D. F. In "Computer Programs for Chemistry"; DeTar, D. F., Ed.; W. A. Benjamin: New York, 1968; Vol. I, pp 126–173. Sliwinski, W. F. Ph.D. Thesis, Princeton University, 1972. (b) Barbe, W. Ph.D. Thesis, University of Freiburg, 1981.

(45) Treatments such as those of ref 23, 24 are applicable only if the variables are separable (Y , N = solvent properties, m , l = substrate properties, with no mixed terms).

alcohols) that need the $l_{4b}NK_L$ term to be correlated. When we observe that the difference in the $N_{K,L}$ parameter between 100% methanol and water (both correlated without $N_{K,L}$) is actually larger than the difference in $N_{K,L}$ between water and any of acetic acid, formic acid, 50, 70, or 97% TFE, which all require $N_{K,L}$ to be correlated, the idea of solvent nucleophilicity playing a role in the solvolysis of *tert*-butyl chloride (**4b**) loses all strength.⁵² The lN term becomes then simply an adjustable correction needed to bring a certain set of solvents on the mY correlation. The "cruel trick"^{53a} is that normally the decrease in nucleophilicity (expressed by a negative N) is paralleled by an increase in electrophilicity, which is incorporated in Y .^{24,33,34g,35} Since the Y values are obtained from rates of adamantyl substrates (**1**), the *tert*-butyl substrates (**4**), less susceptible to electrophilic assistance, fall off the mY line. The effect of increased electrophilic solvent assistance in **1** is then taken as an effect of nucleophilic assistance in **4**.

C. Nucleophilic solvent participation has been claimed for the solvolysis of *tert*-butyldimethylsulfonium salts (**5**).^{53,54} (Inter-

estingly, electrophilic solvent assistance is considered in that work to be the dominant factor for *tert*-butyl chloride solvolysis.^{53a}) It must be noted, however, that the sulfonium cation can undergo nucleophilic attack not only at the *tert*-butyl group but also at a methyl group. Indeed, not only is the attack at methyl statistically favored by a factor of 2 but the reactivity of methyl group toward attack by a nucleophile is very much higher than that of a *tert*-butyl group.⁵⁵ Therefore, nucleophilic solvent attack at the methyl group should (a) be visible in the reaction kinetics and (b) lead to a significant amount of methyl *tert*-butyl sulfide as a product. If a sizable amount of the latter compound is not formed,⁵⁶ the idea of nucleophilic assistance in the solvolysis of **5** cannot be sustained.

Acknowledgment. We are indebted to Dennis N. Kevill, T. William Bentley, and John S. Lomas for helpful comments. Helpful discussions with Hans-Dieter Beckhaus concerning the molecular mechanics calculations are also acknowledged.

Registry No. **1a**, 97645-21-1; **1e**, 768-95-6; **1f**, 6221-75-6; **2a**, 97645-22-2; **2e**, 31061-64-0; **3a**, 97654-82-5; **3a**, 14504-80-4; **4a**, 1559-07-5; **4e**, 75-65-0; **5**, 52956-50-0; **6**, 31083-61-1; **7**, 5511-18-2; **8**, 17768-41-1; MeLi, 917-54-4; $CF_3(CF_2)_2C(O)Cl$, 375-16-6; 1-homoadamantanecarboxylic acid, 31061-65-1; 1-adamantanecarboxylic acid, 828-51-3.

(54) The discussion of this reaction was requested by a reviewer of the manuscript.

(55) Ingold, C. K. In "Structure and Mechanism in Organic Chemistry"; Cornell University Press: Ithaca, NY, 1969; pp 428-436.

(56) Kevill, D. N., personal communication.

(52) A sound physical model involving nucleophilic assistance would require that rates in nonnucleophilic solvents be correlated by the two-parameter equation $\log(k/k_0) = m_{4b}Y$, while for the nucleophilic solvents the deviation be measured by the $l_{4b}N$ term. This approach can be followed intuitively better if HFIP is taken as the reference solvent ($Y = 0, N = 0$), thus moving the origin along the coordinate axes without otherwise affecting the correlation. Inapplicability of this approach casts doubts on the mechanism involving nucleophilic solvent participation for **4b**.

(53) (a) Kevill, D. N.; Kamil, W. A.; Anderson, S. W. *Tetrahedron Lett.* **1982**, *23*, 4635. (b) Kevill, D. N.; Anderson, S. W. Seventh IUPAC conference on Physical Organic Chemistry, Auckland, New Zealand, 20-24 Aug, 1984; Abstract C2.

2-Azapyrylium Salts from Aluminum Halide σ Complexes of Cyclobutadienes and NOCl. On the Possible Intermediacy of a Heteroatom-Substituted Pyramidal Cation

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Abstract: Di-, tri-, and tetraalkyl-2-azapyrylium salts have been obtained in high yield from the reaction of dialuminum hexahalide σ complexes of di-, tri-, and tetraalkylcyclobutadienes with NOCl. The structure of 3,4,5,6-tetramethyl-2-azapyrylium tetrachloroaluminate (**19**) has been studied in the crystalline phase by X-ray crystallography. On the basis of the ¹H and ¹³C NMR, UV, and X-ray data, it is concluded that the 2-azapyrylium ion is a flat, aromatic ring system. From a consideration of bond energies and from the crystallographically determined structure, it follows that **20A** is the most important canonical form contributing to the actual structure of the 2-azapyrylium moiety. The reaction of complexes **6** (Al₂Br₆) and **7** (Al₂Br₆) with NOCl yields in both cases two isomeric 2-azapyrylium salts: **15r/15u** and **16r/16u**, respectively. The substitution pattern of the alkyl groups in **15r** and **16r** is not the same as in the precursor cyclobutadiene Al₂Br₆ σ complexes. A reaction mechanism is proposed to account for the formation of rearranged and unrearranged 2-azapyrylium salts. Finally, the possible intermediacy of the heteroatom-substituted pyramidal cation **28** in this reaction is discussed. On the basis of a comparison of the relevant orbital energies and the principle of isolobality, it is argued that the heteroatom-substituted pyramidal cation **28**, with NO⁺ in the apex and cyclobutadiene as the base of the pyramid, is more likely to exist than the long-sought pyramidal cyclobutadiene-CO complex.

Alkyl-substituted σ -aluminum halide cyclobutadiene complexes react with carbon-carbon and carbon-nitrogen triple-bond-containing reagents¹ to yield benzene² and pyridine³ derivatives (exemplified in Scheme I⁴). We thought it feasible to extend the scope of the reaction scheme by using (positively charged)

heteroatom-heteroatom triple-bond-containing reagents. Use of either of these reagents or of compounds which can be regarded

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(1) For a review of these synthetic applications, see: Hogeveen, H.; Kok, D. M. "The Chemistry of Triple-Bonded Functional Groups"; Patai, S., Rappoport, Z., Eds.; Wiley, Chichester, UK, 1983; Suppl. C, Part 2, Chapter 23.

(2) Koster, J. B.; Timmermans, G. J.; van Bekkum, H. *Synthesis* **1971**, 139. Hogeveen, H.; Jorritsma, H.; Wade, P. A. *Tetrahedron Lett.* **1974**, 3915. Driessen, P. B. J.; Hogeveen, H. *J. Organomet. Chem.* **1978**, *156*, 265.