(MeOH) 221 nm (ϵ 27,700), 260 (9530), and 361 (9190); nmr (CDCl$_3$) δ 1.17 (s, 6 H), 2.60 (d, J = 5 Hz, 2 H), 2.65 (s, 2 H), 3.63 (s, 2 H), 3.73 (s, 6 H), 4.03 (t, J = 5 Hz, 1 H), 4.83 (s, 2 H), 7.33 ppm (m, 5 H); mass spectrum m/e M$^+$ 480, base 354.

Anal. Calcd for $C_{23}H_{26}N_2O_5Cl_2$: C, 57.39; H, 5.44; N, 5.82; Cl, 14.73. Found: C, 57.44; H, 5.16; N, 5.78; Cl, 14.84.

The less polar, yellow band immediately above the band due to **8** provided **9:** 37% yield (202 mg); mp 175.5–175.6°; ir (CHCl$_3$) 2935, 1675, 1620, 1535, 1425, 1228, 1143 cm^{-1}; λ_{max} (MeOH) 223 nm (ϵ 32,400), 274 (13,800), and 380 (8420); nmr (CDCl$_3$) δ 1.10 (s, 3 H), 1.17 (s, 3 H), 2.50 (m, 2 H), 3.27 (br d, J = 5 Hz, 1 H), 3.50 (br d, J = 5 Hz, 1 H), 3.67 (s, 2 H), 3.73 (s, 6 H), 4.97 (m, 1 H), 5.09 (d, J = 7.5 Hz, 1 H), 5.45 (d, J = 7.5 Hz, 1 H), 7.37 (m, 3 H), 7.67 ppm (m, 2 H); mass spectrum m/e M$^+$ 480, base 354.

Anal. Calcd for $C_{23}H_{26}N_2O_5Cl_2$: C, 57.39; H, 5.44; N, 5.82; Cl, 14.73. Found: C, 57.48; H, 5.11; N, 5.79; Cl, 14.86.

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Registry No.—**1,** 51898-97-6; **2,** 24423-88-9; **3,** 3317-61-1; **4,** 6931-11-9; **5,** 51849-12-8; **6,** 51849-13-9; **8,** 51849-14-0; **9,** 51849-15-1.

References and Notes

(1) U. Eisner and J. Kuthan, *Chem. Rev.*, **72,** 1 (1972).

(2) W. von E. Doering and W. E. McEwen, *J. Amer. Chem. Soc.*, **73,** 2104 (1951); S. Weber, H. L. Slates, and N. L. Wendler, *J. Org. Chem.*, **32,** 1668 (1967); D. L. coffen, *J. Org. Chem.*, **33,** 137 (1968); F. DiNinno, Jr., W. L. Heckle, Jr., D. K. Rehse, and R. M. Wilson, *Tetrahedron Lett.*, 2639 (1972); H. Ahlbrecht and F. Kröhnke, *Justus Liebigs Ann. Chem.* **704,** 133 (1967); **717,** 96 (1968); T. Severin, H. Lerche, and D. Bätz, *Chem. Ber.*, **102,** 2163 (1969); R. E. Lyle and G. J. Ganthier, *Tetrahedron Lett,* 4615 (1965); R. E. Lyle and E. White, V, *J. Org. Chem.*, **36,** 772 (1971); V. Mann, G. Schneider, and F. Krönke, *Tetrahedron Lett.*, 683 (1973).

(3) J. Kuthan and E. Janečková, *Collect. Czech. Chem. Commun.*, **29,** 1654 (1964).

(4) J. Hamer and A. Macaluso, *Chem. Rev.*, **64,** 473 (1964).

(5) The *N*-(2,6-dichlorobenzyl)-3,5-dicarbomethoxypyridinium tosylate (mp 162.7–162.8°) was prepared from 3,5-dicarbomethoxypyridineand 2,6-dichlorobenzyl *p*-toluenesulfonate (mp 97.6–97.8°).

(6) J. Thesing and W. Sirrenberg, *Chem. Ber.*, **92,** 1748 (1959).

(7) R. Bonnett, R. F. C. Brown, V. M. Clark, I. O. Sutherland, and A. Todd, *J. Chem. Soc.*, 2094 (1959).

Structural Analysis by Lanthanide-Induced Shifts. V.[1] Influence of Steric and Conjugative Effects on the Barriers to Rotation in *N*,*N*-Dimethylamides

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Dynamic nuclear magnetic resonance (dnmr) is one of the most powerful tools for the evaluation of rate constants and of the free-energy barriers to rotation (ΔG^*),[2] and the relative simplicity of this technique encourages a systematic search in order to assess the relative merits of steric and conjugative effects on the barriers to internal rotation in *N*,*N*-dimethylamides.[3-7]

However, this task is somewhat hampered by the necessity of using different solvents in dnmr work, in order to overcome solubility problems and the accidental isochrony of signals in a given solvent. Solvent effects on the barrier height are in fact of an order of magnitude comparable to steric or conjugative effects.[7]

The latter difficulty represented a serious problem also in our case since, in our hands, several of the amides studied by us yielded CDCl$_3$ spectra unsuitable for the measurement of ΔG^* at the coalescence point.

The use of lanthanide shift reagents (LSR) to simplify the amide spectra[8,9] offers a convenient way to avoid uncertainties caused by comparing data obtained in different solvents. Our results, in agreement with those of other authors,[10,11] show that the use of Eu(fod)$_3$ at low shift reagent/substrate molar ratios does not affect sensibly the ΔG^*. This fact allowed us to measure the ΔG^* of a series of structurally related *N*,*N*-dimethylamides in the same solvent (CDCl$_3$), even if some of the compounds studied exhibited accidental isochronous methyl signals in the undoped spectra.

The resulting set of immediately comparable data has provided detailed information on the relative strength of conjugative effects of some unsaturated amides. For instance, it can be inferred that the conjugative power of the phenyl group is intermediate between that of furan and thiophene, and that the vinyl and cyclopropyl groups are about as "strong" as furan. Furthermore, in some cases, differences in ΔG^* could be attributed to finer conformational effects.

Results

In Tables I and II are reported the results of our measurements, performed on two series of structurally related amides and diamides.

For some compounds in Table I, our ΔG^* estimates in the absence of LSR are in good agreement with data already available in the literature (references in the last column in Table I). The addition of Eu(fod)$_3$ at low shift reagent/substrate molar ratios does not affect sensibly the ΔG^*, but it does increase the separation of the diastereotopic *N*-methyl signals.

The advantage of performing coalescence measurements on peaks well resolved at low temperature is obvious. However, although the peak separation may be varied at will by increasing the amount of LSR, in our experience the optimal separation ranges between 15 and 60 Hz, corresponding to a molar ratio Eu(fod)$_3$/amide of *ca.* 0.1–0.2. Higher separations cause expand of uncertainties in the T_c estimates.

Despite the experimental evidence produced here that, in several cases, measurements of barriers with and without the LSR produces sensibly the same result, *it cannot be inferred that the LSR does not affect the barrier to rotation in the complexed substrate.* In fact, quite recently, in the case of trimethyl carbamate,[11] experiments performed at increasing shift reagent/substrate molar ratios have shown that the observed rate constant is the weighted average for isomerization of free and complexed substrate and, by extrapolation, it was possible to estimate the ΔG^* for both processes (the free-energy difference is about 2.5 kcal/mol.[11]

Of course, using *low* shift reagent/substrate molar ratios, only a small amount of complex is formed (most of the amide being present in the free state), so that our findings seem quite reasonable.

Discussion

Structural effects on the barrier to internal rotation in amides have been acknowledged in the recent literature.[3-7]

Considering the resonance structures I and II as possible contributors to the planar ground state of *N*,*N*-dimethyl-

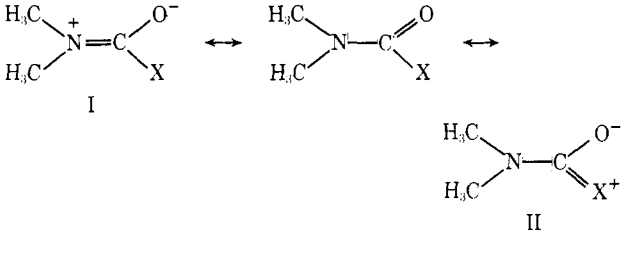
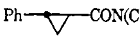
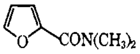
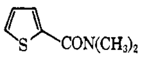
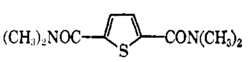
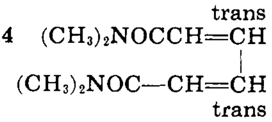
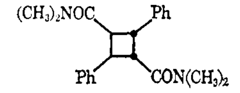
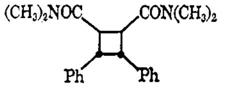
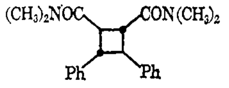
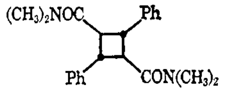
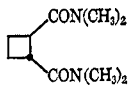


Table I
Barrier Heights to Site Exchange in Various N,N-Dimethylamides Measured in the Presence or Absence of Eu(fod)$_3$

	Compd	Registry no.	Molar ratio of Eu(fod)$_3$ to amide	$\Delta\nu$, Hz	ΔG^*,[a] kcal mol^{-1}	T_c, °C	Ref[b]
1	$CH_3CON(CH_3)_2$	127-19-5	0 0.08	6.0 18.5	18.4 18.3	71 83	3, 7, 8
2	$CH_2{=}CHCON(CH_3)_2$	2680-03-7	0 0.10	c 40.0	 16.9	 65.5	
3	$PhCH{=}CHCON(CH_3)_2$	13156-74-6	0 0.16	c 56.8	 16.5	 63	5b, 5c, 6
4	$CH_2{=}C(CH_3)CON(CH_3)_2$	6976-91-6	0 0.09	4.5 31.0	15.6 15.8	16.5 41	
5		17696-23-0	0 0.10	c 27.0	 16.6	 54.5	5d
6		35682-53-2	0 0.21	6.0 61.5	 17.0	 73	5d
7		5279-83-4	0 0.12	13.0 16.0	16.6 17.1	47 58	5d
8	$PhCON(CH_3)_2$	611-74-5	0 0.13	7.8 59.5	15.8 15.9	26 51	4, 5a, 5b, 5c
9	$(o\text{-}CH_3)PhCON(CH_3)_2$	6639-19-6	0 0.12	18.0 55.0	18.0 17.8	76 87.5	
10		13156-75-7	0 0.13	c 42.5	 16.8	 26	
11		30717-57-8	0 0.15	c 41.5	 14.1	 12	
12		51869-10-4	0 0.18	c 45.5	 14.3	 17.5	
13	$(CH_3)_2NOCCH{=}CHCON(CH_3)_2$ trans	17878-64-7	0 0.12	6.0 13.8	17.8 17.7	63 68.5	
14	 $\begin{matrix}\text{trans}\\(CH_3)_2NOCCH{=}CH\\ \vert\\(CH_3)_2NOC{-}CH{=}CH\\ \text{trans}\end{matrix}$	51869-47-7	0 0.14	c 30.5	 16.8	 60	

[a] ΔG^* measured at T_c. [b] References leading to ΔG^* data from other authors (determined in absence of LSR). [c] Accidental isochronous signals, in the experimental conditions (see Experimental Section).

Table II
Barrier Heights for Some Cyclobutanedicarboxamides Measured in the Presence or Absence of Eu(fod)$_3$

	Compd	Registry no.	Molar ratio of Eu(fod)$_3$ to amide	$\Delta\nu$, Hz	ΔG^*,[a] kcal mol^{-1}	T_c, °C
1		51869-48-8	0 0.20	2.0 12.0	 19.2	 93
2		51869-49-9	0 0.25	7.5 17.7	17.5 17.6	57 69
3		51898-47-6	0 0.23	9.5 30.5	18.7 18.5	82 94
4		51898-48-7	0 0.18	21.0 51.0	17.4 17.5	68 81
5		51936-10-8	0 0.12	4.5 20.5	18.5 18.2	68 82

[a] ΔG^* measured at T_c.

amides and assuming the transition state to be one in which the -COX moiety has been twisted out of planarity by 90°, the magnitude of the torsional barrier will depend on the relative weight of structures I and II, respectively.

In fact, when X is an aliphatic group, structure I contributes to a high degree to the above resonating systems and the partial double-bond character of the ground state will therefore result increased. On the other side, when X is a strong electron-donating group, structure II becomes more important and the partial double-bond character of the ground state will be reduced.

The measured torsional barrier will therefore reflect the

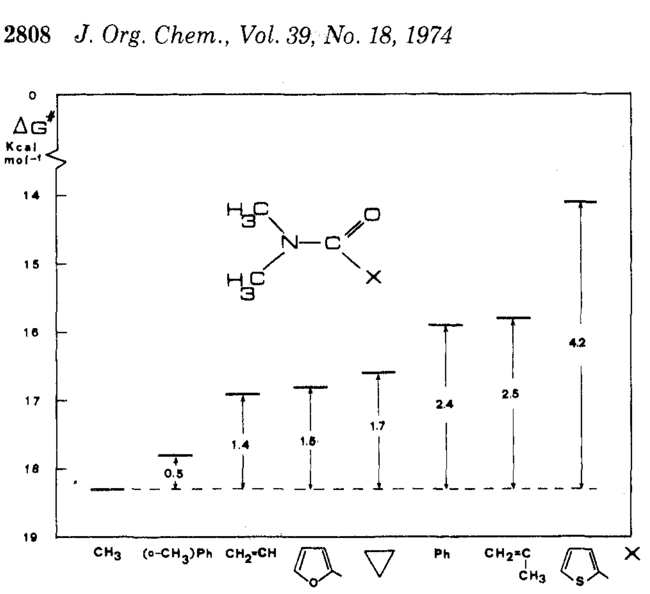


Figure 1. Energy barriers to internal rotation for some *N,N*-dimethylamides (see text for discussion).

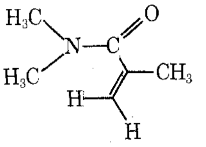
relative contributions of structures I and II in the resonating system.

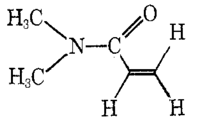
Within this theoretical framework, the diagram in Figure 1 serves well to illustrate some of the salient features coming from the analysis of the ΔG^* data in Table I. Since the highest torsional barrier is that of DMA (X = CH_3), one can assume that the energy barrier lowering in the remaining compounds is a measure of the ability of a specific substituent to interact with the amide carbonyl group (conjugative power).

In fact, the energy differences observed (Figure 1) for the various substituents are in close correspondence with their relative *conjugative power,* as it can be deduced from the general qualitative picture coming from studies with different techniques.

Furthermore, an interesting effect is observed in aromatic amides (compounds **8-12,** Table I). The conjugative power of the phenyl group is found to be intermediate between that of furan and thiophene, while in compound **9** (where the ortho methyl group hinders the molecular planarity) the ΔG^* rises almost to the level of DMA. It has to be noted that these observations could not be done working in absence of LSR, since both furan and thiophene amides yield accidental isochronous methyl signals in $CDCl_3$ (Table I).

Finally, data in Table I and Figure 1 indicate that α-methyl substitution lowers the ΔG^* in compound **4** with respect to compound **2.** This effect may be ascribed to the different conformational preference adopted by these two molecules. Compound **4** was reported to adopt predominantly the s-trans form[12,13] (III); in contradistinction compound **2** exists predominantly in the s-cis conformation[12,13] (IV).


III


IV

Therefore, the ΔG^* *difference observed should reflect* the relative conjugative power of the two forms, and the s-trans conformation is known[14] to be favored in this respect.

Data in Table II further illustrate the reliability of the ΔG^* estimates in the presence of LSR, and also disclose a small but definite ΔG^* difference between cyclobutane cis diamides (compounds **2** and **4,** Table II) and the corresponding trans diamides (compounds **1, 3,** and **5,** Table II).

This difference is possibly due to some steric hindrance and/or induced local field effects of the two amide groups in the cis position.

Experimental Section

Spectra. The ^1H nmr spectra were recorded on a Varian A-60D spectrometer equipped with variable-temperature accessories. Temperature measurements were based on the chemical shift separation of the protons of an ethylene glycol or methanol sample, and utilized the temperature-shift correlation of Van Geet.[15] T_c values in Tables I and II represent the average of several measurements.[16] The Gutowsky-Holm[16] approximation was used in order to calculate the rate constants for the site exchange; these rates were employed to derive the free energies of activation (ΔG^*) from the Eyring equation, at the coalescence temperature. The estimated error in the ΔG^* values reported is ±0.2 kcal/mol based almost exclusively on uncertainties in T_c.

Eu(fod)$_3$ was added from a stock solution (0.32 *M*) with the help of a 50-μl microsyringe to a ~5% $CDCl_3$ solutions of amide (TMS as internal reference).

Synthetic. *N,N*-Dimethylacetamide (compound **1,** Table I) was a commercial product (Aldrich) and was distilled under reduced pressure before use. The following amides were prepared according to the interfacial condensation procedure described below and characterized according to the literature: amides **2,**[17] **3,**[18] **4,**[19] **5,**[20] **6,**[21] **7,**[5d] **8,**[18] **9,**[22] **10,**[23] **11,**[24] and **13**[25] in Table I and amide **3** in Table II.[26] The amides **12** and **14** in Table I and **1, 2, 4,** and **5** in Table II were hitherto unreported and in Table III are summarized their physical and chemical characteristics.

Table III
Physical and Chemical Characteristics of Some Diamides[a]

Compd	Mp, °C	Recrystn solvent	Formula
12[b]	125–126	Acetone	$C_{10}H_{14}N_2O_2S$
14[b]	224–225	Ethanol–water	$C_{10}H_{16}N_2O_2$
1	204–205	Benzene	$C_{22}H_{26}N_2O_2$
2[c]	158–159	Benzene	$C_{22}H_{26}N_2O_2$
4[c]	109–110	Hexane–benzene	$C_{22}H_{26}N_2O_2$
5[c]	85–86	Petroleum ether	$C_{10}H_{18}N_2O_2$

[a] Satisfactory analytical values (±0.3% for C, H, N) were reported for all compounds in table: Ed. [b] See Table I. [c] See Table II.

A 0.01-mol portion of acid chloride[27] dissolved in dry ether or benzene and 0.01 mol of dimethylamine hydrochloride (Aldrich) dissolved in water were mixed under stirring in a blender jar. While the mixture was rapidly stirred, a solution of 0.02 mol of sodium hydroxide in water was added dropwise. The temperature was then raised for 30 min. The reaction mixture was poured onto crushed ice, and the organic layer was extracted with chloroform. The solvent was removed under reduced pressure and the crude product was distilled under vacuum or recrystallized from opportune solvent and vacuum dried (see Table III).

Registry No.—Eu(fod)$_3$, 17631-68-4.

References and Notes

(1) Part IV of this series submitted for publication.
(2) (a) G. Binsch, *Top. Stereochem.,* **3,** 97 (1968); (b) H. Kessler, *Angew. Chem., Int. Ed. Engl.,* **9,** 219 (1970); (c) D. Kost, E. H. Carlson, and M. Raban, *Chem. Commun.,* 656 (1971).
(3) W. E. Stewart and T. H. Siddall, *Chem. Rev.,* **70,** 517 (1970).
(4) L. M. Jackman, T. E. Kavanagh, and R. C. Haddon, *Org. Magn. Resonance,* **1,** 109 (1969).
(5) (a) K. Spaargaren, P. K. Korver, P. J. Van der Haak, and T. J. De Boer, *Org. Magn. Resonance,* **2,** 295 (1970); (b) *ibid.,* **3,** 605 (1971); (c) *ibid.,* **3,** 615 (1971); (d) *ibid.,* **3,** 639 (1971).
(6) S. L. Spassov, V. S. Dimitrov, M. Agova, I. Kantschowska, and R. Todorova, *Org. Magn. Resonance,* **3,** 551 (1971).
(7) T. Drakenberg, K. I. Dahlqvist, and S. Forsen, *J. Phys. Chem.,* **76,** 2178 (1972).
(8) G. Montaudo and P. Finocchiaro, *J. Org. Chem.,* **37,** 3434 (1972).
(9) C. Beautè, Z. W. Wolkowski, and N. Thoai, *Chem. Commun.,* 700 (1970).

(10) H. N. Cheng and H. S. Gutowsky, *J. Amer. Chem. Soc.*, **94**, 5505 (1972).

(11) S. R. Tanny, M. Pickering, and C. S. Springer, *J. Amer. Chem. Soc.*, **95**, 6227 (1973).

(12) C. Kruk and K. Spaargaren, *Spectrochim. Acta, Part A*, **27**, 77 (1971).

(13) G. Montaudo, V. Librando, S. Caccamese, and P. Maravigna, *J. Amer. Chem. Soc.*, **95**, 6365 (1973).

(14) D. D. Faulk and A. Fry, *J. Org. Chem.*, **35**, 364 (1970).

(15) A. L. Van Geet, *Anal. Chem.*, **42**, 679 (1970); **40**, 2227 (1968).

(16) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(17) W. P. Ratchford and C. H. Fisher, *J. Amer. Chem. Soc.*, **69**, 1911 (1947).

(18) H. Staudinger and N. Kon, *Justus Liebigs Ann. Chem.*, **384**, 38 (1911).

(19) W. P. Ratchford, J. H. Lengel, and C. H. Fisher, *J. Amer. Chem. Soc.*, **71**, 647 (1949).

(20) E. Renk, P. R. Shafer, W. Graham, R. H. Mazur, and J. D. Roberts, *J. Amer. Chem. Soc.*, **83**, 1987 (1961).

(21) J. Smejkal and J. Farkas, *Collect. Czech. Chem. Commun.*, **28**, 404 (1963).

(22) L. van Scherpenzel, *Recl. Trav. Chim. Pays-Bas*, **20**, 149 (1897).

(23) R. J. Meltzer, A. D. Lewis, and J. A. King, *J. Amer. Chem. Soc.*, **77**, 4062 (1955).

(24) U. Michael and A. B. Hornfeldt, *Tetrahedron Lett.*, 5219 (1970).

(25) F. Ascoli Marchetti and M. L. Stein, *Gazz. Chim. Ital.*, **84**, 816 (1954).

(26) R. Stoermer and E. Emmel, *Chem. Ber.*, **53**, 497 (1920).

(27) All the acid chlorides were prepared from the corresponding acids by treatment with thionyl chloride and their characteristics were coincident with those reported in the literature.

Hydrogen Bonding. III. Tetrapropylammonium Hydrogen Difluoride and the Thermal Elimination Reaction of Tetrapropylammonium Fluoride Hydrates[1]

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Received February 5, 1974

Results

In the course of studies of strongly hydrogen bonded water–anion species in tetraalkylammonium ion salt hydrates[2] we have prepared the lower hydrates of tetrapropylammonium fluoride. Removal of water from an aqueous solution of the fluoride at minimum temperatures with prolonged drying *in vacuo* gives successively the hexa-, tri-, and dihydrates; these substances are low-melting white solids which exist as crystalline slushes at room temperature. Additional water cannot be removed from the dihydrate without a concurrent Hofmann-type elimination reaction occurring.

Miller, Fried, and Goldwhite[3] have suggested that fluoride ion may function as a base in the Hofmann elimination from the observation that some ethylene, triethylamine, and residual acid are formed on extended drying of tetraethylammonium fluoride; this appears to be the only report[4] of fluoride ion functioning in this manner. We find that rapid heating of the tetrapropylammonium fluoride tri- or dihydrates to 140° *in vacuo* results in a smooth and quantitative conversion to propene, tripropylamine, and tetrapropylammonium hydrogen difluoride.

$$2(C_3H_7)_4N^+F^- \cdot 2H_2O \rightleftharpoons (C_3H_7)_3N + C_3H_6 + (C_3H_7)_4N^+HF_2^- + 4H_2O \quad (1)$$

The apparently anomalous generation of a strong acid and a fairly strong base from a neutral substance, that is, the formation of the hydrogen difluoride and tripropylamine instead of tripropylammonium fluoride, is not unexpected in light of our observations[5] on *p*-toluidinium fluoride, which is also thermodynamically unstable relative to the hydrogen difluoride and free amine. The formation of the strongly hydrogen bonded hydrogen difluoride anion provides the driving force to shift these equilibria.

Experimental Section

Eastman Kodak White Label 10% tetrapropylammonium hydroxide solution and Baker reagent grade 48% hydrofluoric acid were used as supplied. Fluoride was determined by precipitation as PbClF. Infrared spectra were recorded on a Beckman IR-12 using NaCl and Nujol mulls. The hydrates were handled under dry nitrogen at all times; polyethylene labware was used in all reactions.

Hydrates of Tetrapropylammonium Fluoride. A. Hexahydrate. A solution of tetrapropylammonium hydroxide (1.031 g, 5.07 mmol) in water (10 ml) was brought to pH 7.00 by addition of hydrofluoric acid. The solvent water was removed *in vacuo* with a rotary evaporator at room temperature for 28 hr. This afforded a white, low-melting (about 30°) crystalline mass containing a quantity of water (0.549 g, 30.5 mmol) corresponding to 6.01 mol of water for each mole of tetrapropylammonium fluoride.

B. Dihydrate. Additional heating of the hexahydrate sample from A *in vacuo* at 55° for 24 hr reduced the water content to 3.64 mol of water per mole of salt. The sample was then heated *in vacuo* at 80° for 1 hr to give a white, semicrystalline slush containing a quantity of water (0.190 g, 10.5 mmol) corresponding to 2.08 mol of water for each mole of tetrapropylammonium fluoride. Titration with base showed a negligible amount of residual acid.

C. Trihydrate. A solution of tetrapropylammonium fluoride (1.036 g, 5.07 mmol) in water (about 15 ml) was prepared exactly as in A. The solvent water was removed *in vacuo* with a rotary evaporator at room temperature for 24 hr, and then the resulting hexahydrate was heated *in vacuo* at 35° for 60 hr. This afforded a white, semicrystalline slush containing a quantity of water (0.273 g, 15.1 mmol) corresponding to 2.99 mol of water for each mole of tetrapropylammonium fluoride.

Elimination Reaction of Tetrapropylammonium Fluoride. A flask containing a crystalline slush of tetrapropylammonium fluoride (1.507 g, 7.329 mmol) and water (0.477 g, 26.5 mmol), which had been prepared as in B above, was connected to a Dry Ice cooled trap fitted with inlet and outlet stopcocks and a fitting to attach an infrared gas cell. The flask was heated rapidly to about 140°, at which point a vigorous decomposition set in. In a few minutes the slush had changed to a hard, white, crystalline mass, with obvious evolution of gas. The flask was found to contain a 99.0% yield of tetrapropylammonium hydrogen difluoride (0.819 g, 3.63 mmol) as white microcrystals. *Anal.* Calcd fo $C_{12}H_{29}NF_2$: F^-, 16.88; HF, 8.88. Found: F^-, 17.08; HF, 9.10.

The trap was removed from the system and allowed to warm in an ice bath to 0° with the stopcocks closed; it was then opened to an infrared gas cell. The vapor was shown to consist solely of propene, identified by its characteristic infrared spectrum. The trap also contained a mixture of two immiscible liquids with the odor of amine; this strongly basic mixture was rinsed from the trap with water; titration with standard hydrochloric acid showed an 88.75% yield of tripropylamine (0.467 g, 3.253 mmol). In a similar experiment the amine was separated from the water in the trap by use of a fine dropper, and identified by its nmr spectrum: δ ($CHCl_3$) triplet, 2.42, 2.30, 2.18 (area 2); sextuplet 1.75–1.05 (area 2); triplet 0.93, 0.83, 0.72 (area 3).

Identification of the Decomposing Species. A sample of tetrapropylammonium fluoride trihydrate (1.309 g, 5.07 mmol) was connected to the vacuum system with a Dry Ice cooled trap and heated *in vacuo* at 42° for 50 hr. After this time the flask contained 1.127 g of a crystalline slush; the infrared spectrum of this material showed, in addition to cation bands, the characteristic infrared spectra of the dihydrate and the hydrogen difluoride (see Discussion). Titration of the solid with sodium hydroxide showed it to contain a 17.3% yield of tetrapropylammonium hydrogen difluoride (0.098 g, 0.438 mmol).[6] Titration of the amine from the trap showed a 16.5% recovery of tripropylamine (0.60 g, 0.418 mmol). If we assume that the quantity of hydrogen difluoride represents one-half of the tetrapropylammonium ions involved in the decomposition reaction (eq 1) the sample now contains 82.7% of the original cations as tetrapropylammonium fluoride (0.857 g, 4.195 mmol) and by difference a quantity of water (0.172 g, 9.6 mmol) corresponding to 2.2 mol of water per mole of fluoride salt.

Discussion

The hydrates of tetrapropylammonium fluoride are extremely stable species, even though they are not highly