versals in approach *have* been observed with tricyclic ketone 7 (but as noted above, there may be complex reasons for this). We also note, in this connection, the large

7

difference in *Z* preference of chloride ion in its approach to the 5-fluoro-2-methyladamant-2-yl cation described earlier;[2,4a] when this cation is generated with hydrogen chloride in methylene chloride from the alcohol, the ratio is about 5:1, whereas one finds >99:1 if the olefin is used as precursor. The presence of a water molecule in the transition state evidently can greatly reduce the face selectivity of the ion. These facts may serve as a hint that surprises may yet be in store if we assume that face selectivity is not a significant function of nucleophilicity.

Experimental Section

Materials. 5-Fluoroadamantan-2-one,[2] 2-phenyladamantan-2-ol,[7] and 2-(pentafluoroethyl)adamantan-2-ol[6] were prepared as described in the literature. The Grignard reagents were prepared in well-dried THF at room temperature (to minimize self-coupling); the ketone was added at room temperature, and the mixture was left for 12–24 h. After concentration, the residues were sampled for analysis; the rest was flash chromatographed over silica with methylene chloride, the *E* alcohols eluted first. The yields varied from 66% to 92%, based on purified materials (the modest yield with *p*-dibromobenzene is due to the formation of bis Grignard reagent which led to difficult to remove byproducts). A complete listing of all ^1H and ^{13}C resonances is given in the supplementary pages. Melting points (uncorrected, in °C): parent alcohols, *p*-NMe_2, 149–150.5; *p*-MeO, 97–99; *p*-Me, 69–70; *p*-Br, 91.5–94; *p*-CF_3, 73–76; 5-fluoro alcohols, *p*-NMe_2, *E* and *Z* not separated; *p*-CF_3 (*E*), 93–94, (*Z*), 112–114; *p*-Br (*E*), 120–122, (*Z*, not available in pure form); *p*-H (*E*), 112–113, (*Z*), 91–93; *p*-Me (*E*), 118–119, (*Z*), 111–113; *p*-MeO (*E*), 131–133, (*Z*), 113–118.

The perfluoroethylation was carried in according to Gassman's general procedure for ketones.[6] The crude mixture upon GC analysis showed the presence of two components with similar retention times; the GC peak ratio was 3.0:1. This same value was obtained also from ^{19}F NMR spectra. Anal. Calcd: C, 49.99; H, 4.90. Found: C, 49.81; H, 4.75. The major isomer crystallized from the residue after some time; it was recrystallized from petroleum ether; mp 100–101 °C. Anal. Calcd: C, 49.99; H, 4.90. Found: C, 49.71; H, 4.94. A detailed list of the ^1H, ^{13}C, and ^{19}F NMR data is appended as supplementary material.

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Supplementary Material Available: Listing of spectral data (MS, IR, ^1H NMR, and ^{13}C NMR) of the six para-substituted 2-phenyl-2-adamantanols and the 14 product adamantanols reported (20 pages). Ordering information is given on any current masthead page.

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Direct Conversion of Long-Chain Carboxamides to Alkylammonium Tosylates with Hydroxy(tosyloxy)iodobenzene, a Notable Improvement over the Classical Hofmann Reaction

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The conversion of carboxamides in aqueous alkaline hypohalite to amines possessing one less carbon atom was first reported by Hofmann in 1881[1] and is a useful and general transformation.[2] However, linear aliphatic amides **1** with R greater than C_9 give little or no amine and are largely diverted to *N*-alkyl-*N'*-acylureas **2**.[2,3] The use of dioxane as cosolvent affords some advantage. Thus, amine yields of nearly 50% from lauramide (R = C_{11}) and tridecanamide (R = C_{12}) with hypochlorite in 33% dioxane have been reported, but it was noted in the same paper that "a run with palmitamide was a complete failure".[4] Until now, the indirect procedure of Jeffreys has been the method of choice for the production of amines from long-chain amides; in methanolic hypohalite, the amides give urethanes **3** from which the amines can be liberated by hydrolysis.[2,4-6]

$\underset{\mathbf{1}}{RCONH_2}$ $\underset{\mathbf{2}}{RNHCONHCOR}$ $\underset{\mathbf{3}}{RNHCOOCH_3}$

In recent years, the utility of hypervalent organoiodine compounds as Hofmann reagents has been recognized.[7-10] However, except for one example (R = C_{11}, 57% yield),[10] they have not been applied to long-chain amides. Our efforts have focused on hydroxy(tosyloxy)iodobenzene (**4**, HTIB), which reacts with carboxamides in *acetonitrile* to give alkylammonium tosylates (eq 1).[10] Such transfor-

$$\underset{\mathbf{4},\ \mathrm{HTIB}}{RCONH_2 + PhI(OH)OTs} \xrightarrow[\Delta]{\mathrm{MeCN}} RNH_3^+,\ OTs^- + PhI \qquad (1)$$

mations proceed through intermediate *N*-phenyliodoniocarboxamide tosylates **5** and their collapse to alkyl isocyanates **6**, *p*-toluenesulfonic acid, and iodobenzene.[11]

$\underset{\mathbf{5}}{RCONH^+IPh,\ OTs^-}$

$\underset{\mathbf{6}}{RN{=}C{=}O}$ $\underset{\mathbf{7}}{CH_3(CH_2)_nCH_2CH_2NH_3^+,\ OTs^-}$

We now report that HTIB is particularly useful for the degradation of long-chain amides. Not only are alkylammonium tosylates obtained in high yields, but the reaction and workup procedures are efficient and simple,

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Table I. Conversion of Long-Chain Carboxamides, $RCONH_2$, to Alkylammonium Tosylates, $R^+NH_3^-OTs$, with Hydroxy(tosyloxy)iodobenzene in Acetonitrile[a]

R	yield,[b] %	R	yield,[b] %
$CH_3(CH_2)_{11}$	90	$CH_3(CH_2)_{16}$	89.5
$CH_3(CH_2)_{12}$	81	$CH_3(CH_2)_{20}$	94
$CH_3(CH_2)_{13}$	91	*trans*-$CH_3(CH_2)_7CH{=}CH(CH_2)_7$	80
$CH_3(CH_2)_{14}$	88		
$CH_3(CH_2)_{15}$	91	*cis*-$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}$	63

[a] The reactions were conducted with 3.00 mmol each of amide and HTIB except for the reaction with docosanamide (2.93 mmol). [b] Rounded off to nearest percent.

especially when compared to those of the classical Hofmann reaction.[2] For example, palmitamide (3.00 mmol, R = C_{15}) was added as the solid to a hot (ca. 65 °C), yellow solution of HTIB (3.00 mmol) in MeCN. After 2 min of heating, the resulting colorless solution was set aside at room temperature whereupon *n*-pentadecylammonium tosylate separated and was isolated in 88% yield. Similar conversions of eight other saturated and unsaturated long-chain amides (R = C_{12}–C_{21}) to alkylammonium tosylates were conducted and are summarized in Table I. The reactions of the saturated amides were apparently more efficient, but the unsaturated ammonium salts were still obtained in good yields.

In addition to the methyl singlet and AA'BB' multiplet of the tosylate ion, the 300-MHz ^1H NMR spectra of the saturated alkylammonium tosylates **7** typically exhibit a broad "singlet" in the aromatic region (NH_3^+) and well-separated multiplets for the methyl group of the carbon chain and each of the two methylene groups closest to nitrogen. The $(CH_2)_n$ moiety produces a characteristically shaped absorption pattern (δ ca. 1.0–1.4) with two prominent peaks of unequal intensity. The spectra of the unsaturated analogues are similar but include additional multiplets for the allylic and vinylic hydrogens.

The success of the classical Hofmann reaction depends on the capture of intermediate isocyanates **6** with hydroxide ion (or water) and the spontaneous decarboxylation of the carbamic acids thus produced.[2] The formation of ureas from long-chain amides has been attributed to the mutual "extraction" of the isocyanate, the final amine, and "earlier intermediates" from the aqueous medium and the coupling of the isocyanate with species other than hydroxide ion,[4] a phenomenon that should become more pronounced with increasing chain length. It also seems likely that the formation of **2** is encouraged by the basicity of the reaction medium; i.e., the isocyanate is captured either by the anion of the starting amide ($RCONH^-$) or the anion of the first-formed *N*-halo amide ($RCONX^-$). With HTIB in acetonitrile, the solubilities are improved and the reaction medium is mildly acidic, thus precluding the production of anions from **1** and **5**.

In summary, HTIB in acetonitrile is an excellent reagent for the direct conversion of long-chain amides to alkylammonium tosylates, an area where the classical Hofmann breaks down.

Experimental Section

General Methods. 300-MHz ^1H NMR spectra of solutions of the alkylammonium tosylates in $CDCl_3$ were recorded on a Varian Model VXR-300 FT NMR spectrometer. Chemical shifts are expressed relative to $CHCl_3$ at δ 7.25. The terminal methyl group of the alkyl chain and the methylene group directly bound to nitrogen in the alkylammonium tosylates typically give rise to three-line multiplets described herein as triplets even though they may not be classical first-order triplets. 75-MHz ^{13}C NMR spectra were recorded on the same instrument. One ^{13}C spectrum each of a saturated and unsaturated alkylammonium tosylate is reported, chemical shifts being given relative to $CDCl_3$ at δ 77.00. IR spectra (Nujol) were recorded on a Perkin-Elmer Model 597 spectrophotometer and are calibrated with polystyrene (1603 cm^{-1}); wavenumber assignments were estimated visually. The NH_3^+ group of the alkylammonium tosylates produces a broad, relatively featureless IR absorption band usually, but not always, separated from the CH region. Absorption maxima of the NH_3^+ band are reported. Elemental analyses were performed by Micro-Tech Laboratories in Skokie, IL and Atlantic Microlab in Atlanta, GA. All of the alkylammonium tosylates exhibited two distinct "melting points"; i.e., they first "melt" to a wet, gelatinous-looking material that liquifies over a narrow range at a higher temperature. The reported melting points are uncorrected.

Erucamide and octadecanamide were purchased (Aldrich Chemical Co.) and used without further purification. All other amides were prepared from the appropriate carboxylic acids ($SOCl_2$, aqueous NH_3) and recrystallized from methanol.

Except for minor variations, the conversion of tetradecanamide to *n*-tridecylammonium tosylate with HTIB is typical of the experiments summarized in Table I and is described in detail. For the remaining alkylammonium tosylates, only physical, spectral, and analytical data are given. The yields given in this section refer to Table I, but much of the characterization data were acquired on products from prior runs.

***n*-Tridecylammonium Tosylate from Tetradecanamide with HTIB.** A mixture of HTIB (1.176g, 3.00 mmol) and MeCN (20 mL) was stirred and heated (hot plate) until all of the HTIB had dissolved (ca. 65 °C). The yellow solution was momentarily removed from the heat source, and *solid* tetradecanamide (0.682 g, 3.00 mmol) was introduced, 5 mL of MeCN being used for rinsing purposes. After 2 min of additional heating (up to 65–70 °C), the resulting colorless solution was allowed to stand at room temperature whereupon *n*-tridecylammonium tosylate separated as a white, crystalline solid: yield, 0.906 g (81%); mp 95–97 °C, 136–137 °C; IR ca. 3115 cm^{-1} (NH_3^+); ^1H NMR δ 0.87 (t, 3 H), ca. 1.0–1.4 (m, 20 H, prominent peaks at δ 1.11 and 1.24), 1.47 (m, 2 H), 2.35 (s, 3 H), 2.72 (t, 2 H), ca. 7.13–7.8 and 7.62 (AA'BB' m and br s, 7 H). Anal. Calcd for $C_{20}H_{37}NO_3S$: C, 64.65; H, 10.04. Found: C, 64.80; H, 10.10.

Dodecylammonium tosylate: yield, 0.966 g (90%); mp 104–106 °C, 134.5–136 °C; IR ca. 3242 (sh), 3138 and 3058 cm^{-1} (NH_3^+); ^1H NMR δ 0.87 (t, 3 H), ca. 1.0–1.4 (m, 18 H, prominent peaks at δ 1.12 and 1.24), 1.47 (m, 2 H), 2.35 (s, 3 H), 2.72 (t, 2 H), ca. 7.13–7.8 and 7.63 (AA'BB' m and br s, 7 H); ^{13}C NMR ($CDCl_3$) δ 14.08, 21.29, 22.67, 26.38, 27.42, 29.02, 29.35, 29.43, 29.58, 29.64, 31.90, 39.95, 125.89, 128.98, 140.61, 141.29. Anal. Calcd for $C_{19}H_{35}NO_3S$: C, 63.82; H, 9.87. Found: C, 63.92; H, 9.88.

***n*-Tetradecylammonium tosylate**: yield, 1.055 g (91%); mp 97–99 °C, 138–139 °C; IR flat maximum from 3088 to 3168 cm^{-1} (NH_3^+); ^1H NMR δ 0.87 (t, 3 H), ca. 1.0–1.4 (m, 22 H, prominent peaks at δ 1.12 and 1.24), 1.47 (m, 2 H), 2.35 (s, 3 H), 2.71 (t, 2 H), ca. 7.15–7.8 and 7.63 (AA'BB' m and br s, 7 H). Anal. Calcd for $C_{21}H_{39}NO_3S$: C, 65.41; H, 10.19. Found: C, 65.27; H, 10.21.

***n*-Pentadecylammonium tosylate**: yield, 1.058 g (88%); mp 93–94 °C, 138–139 °C; IR ca. 3128 cm^{-1} (NH_3^+); ^1H NMR δ 0.87 (t, 3 H), ca. 1.0–1.4 (m, 24 H, prominent peaks at δ 1.12 and 1.25), 1.47 (m, 2 H), 2.35 (s, 3 H), 2.72 (m, 2 H), ca. 7.15–7.8 and 7.64 (AA'BB' m and br s, 7 H). Anal. Calcd for $C_{22}H_{41}NO_3S$: C, 66.12; H, 10.34. Found: C, 65.80; H, 10.18.

***n*-Hexadecylammonium tosylate**: yield, 1.125 g (91%); mp 98–100 °C, 140–141 °C; IR ca. 3150 and 3050 cm^{-1} (NH_3^+); ^1H NMR δ 0.87 (t, 3 H), ca. 1.0–1.36 (m, 26 H, prominent peaks at δ 1.11 and 1.25), 1.46 (m, 2 H), 2.35 (s, 3 H), 2.71 (t, 2 H), ca. 7.12–7.78 and 7.63 (AA'BB' m and br s, 7 H). Anal. Calcd for $C_{23}H_{43}NO_3S$: C, 66.78; H, 10.48. Found: C, 66.90; H, 10.63.

***n*-Heptadecylammonium tosylate**: yield, 1.148 g (89.5%); mp 93–94 °C, 140–141 °C; IR ca. 3140 cm^{-1} (NH_3^+); ^1H NMR δ 0.87 (t, 3 H), ca. 1.0–1.36 (m, 28 H, prominent peaks at δ 1.12 and 1.25), 1.47 (m, 2 H), 2.35 (s, 3 H), 2.72 (t, 2 H), ca. 7.12–7.77 and 7.64 (AA'BB' m and br s, 7 H). Anal. Calcd for $C_{24}H_{45}NO_3S$: C, 67.40; H, 10.60. Found: C, 67.69; H, 10.34.

***n*-Heneicosylammonium tosylate**: yield, 1.336 g (94%); mp 97–98 °C, 137–138 °C; IR ca. 3128 cm^{-1} (NH_3^+); ^1H NMR δ 0.88 (t, 3 H), ca. 1.07–1.38 (m, 34 H, prominent peaks at δ 1.14 and 1.26), ca. 1.38–1.73 (m's, 4 H), 2.36 (s, 3 H), 2.73 (t, 2 H), ca. 7.13–7.8 and 7.64 (AA'BB' m and br s, 7 H). Anal. Calcd for

$C_{28}H_{53}NO_3S$: C, 69.51; H, 11.04. Found: C, 69.72; H, 11.14.

***trans*-8-Heptadecenylammonium tosylate (from elaidamide)**: yield, 1.019 g (80%); mp 90–95 °C, 126–127 °C; IR ca. 3253 (sh), 3143 and 3053 cm^{-1} (NH_3^+); ^1H NMR δ 0.87 (t, 3 H), ca. 1.0–1.4 (m, 20 H, prominent peaks at δ 1.12 and 1.25), 1.47 (m, 2 H), 1.92 (m, 4 H), 2.35 (s, 3 H), 2.70 (t, 2 H), 5.35 (m, 2 H), ca. 7.15–7.8 and 7.64 (AA'BB' and br s, 7 H); ^{13}C NMR ($CDCl_3$) δ 14.07, 21.28, 22.63, 26.31, 27.40, 28.85, 28.94, 29.17, 29.27, 29.45, 29.53, 29.62, 31.86, 32.50, 32.58, 39.88, 125.85, 128.96, 130.03, 130.42, 140.60, 141.24 (low-intensity resonances at 29.34 and 29.37, impurities?). Anal. Calcd for $C_{24}H_{43}NO_3S$: C, 67.72; H, 10.18. Found: C, 67.67; H, 10.17.

***cis*-12-Heneicosenylammonium tosylate (from erucamide)**: yield, 0.91 g (63%); mp 68–70 °C, 110–113 °C; IR ca. 3245 (sh), 3125 and 3055 cm^{-1} (NH_3^+); ^1H NMR δ 0.87 (t, 3 H), ca. 1.0–1.38 (m, 29 H, (expected, 28 H) prominent peaks at δ 1.12 and 1.25), 1.47 (m, 2 H), 2.00 (m, 3.6 H), 2.35 (s, 3 H), 2.70 (t, 2 H), 5.34 (m, 2 H), ca. 7.12–7.8 and 7.64 (AA'BB' m and br s, 7 H). Anal. Calcd for $C_{28}H_{51}NO_3S$: C, 69.81; H, 10.67. Found: C, 70.06; H, 10.70.

Reaction of *N*-[(Trimethylsilyl)methyl]azinones

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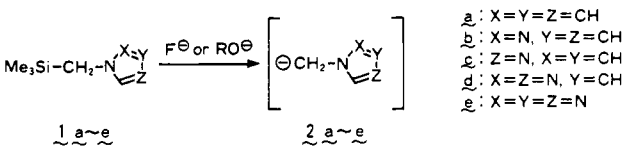
In recent years,[1] we have reported the reaction of carbonyl compounds with azolylmethyl anions **2a–e** derived from the fluoride- or alkoxide-induced desilylation of 1-[(trimethylsilyl)methyl]azoles **1a–e** (Scheme I). The reaction of 1-[(trimethylsilyl)methyl]-1,2,4-triazole (**1d**) with carbonyl compounds in the presence of fluoride catalyst proceeded smoothly, while that of 1-[(trimethylsilyl)-methyl]pyrrole (**1a**) failed. Since the nucleophilic cleavage of C–Si bond is dependent on the stability of the generated carbanion,[2] the difference between **1a** and **1d** was explained by the concept[3] of a dipole-stabilized carbanion. Our interest in this reaction led us to investigate the generation of azinonylmethyl anions **4a–e** by fluoride-induced desilylation of the corresponding *N*-[(trimethylsilyl)methyl]azinones **3a–e** (Scheme II).

Although lithiation of *N*-alkylazinones has been investigated,[4–9] it cannot be used to generate azinonylmethyl anions **4a–e** from the corresponding *N*-methylazinones, except in the case of 1-alkyl-4,6-diphenyl-2-pyridone which is lithiated at N-Cα of the alkyl radical and then made to react with electrophiles.[6]

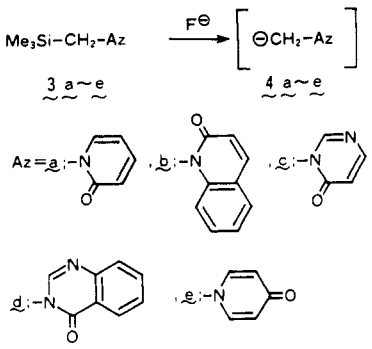
We now report the generation of azinonylmethyl anions **4a–e** derived from the fluoride-induced desilylation of *N*-[(trimethylsilyl)methyl]azinones **3a–e** in the presence of aldehydes and ketones.[10] Also described are the thermal reactions of **3a,e** with ketones and diethyl acetylenedicarboxylate.

Scheme I

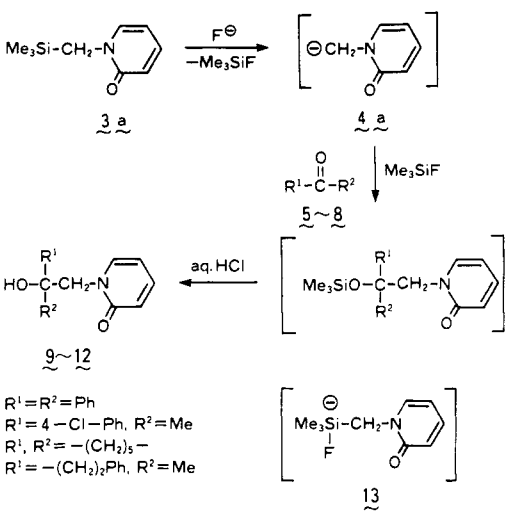


1 a~e 2 a~e

Scheme II



Scheme III



Results and Discussion

Preparation of *N*-[(Trimethylsilyl)methyl]azinones 3a–e. Treatments of 2-pyridone, 2-quinolone, 4-pyrimidinone, and 4-quinazolinone with (chloromethyl)trimethylsilane in the presence of potassium carbonate in dry DMSO led to the (trimethylsilyl)methyl derivatives **3a** (76%), **3b** (64%), **3c** (55%), and **3d** (91%), respectively. The structure of **3c** was confirmed by spectroscopic comparison with 1-methyl-4-pyrimidinone and 3-methyl-4-pyrimidinone[11] and the structure of **3d** was determined by referring to the product of alkylation of 4-quinazolinone.[12] 1-[(Trimethylsilyl)methyl]-4-pyridone (**3e**) was prepared by using a modification of a literature procedure[13] as de-

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