were purchased from PCR, Gainesville, FL. Fluorine was purchased from Air Products.

**Preparation of 3-Methoxy-17-[(trimethylsilyl)oxy]estrone (3).** Diisopropylamine (110 μL, 0.785 mmol) was dissolved in 3 mL of dry THF under $N_2$ atmosphere. The mixture was cooled to 0 °C, and 500 μL (1.00 mmol) of 2 M *n*-butyllithium was added dropwise by syringe. 3-Methyl estrone ether (73 mg, 0.26 mmol) in 5 mL of dry THF was added dropwise by syringe, followed by addition of an excess amount of trimethylsilyl chloride (165 μL, 1.30 mmol). The mixture was stirred at 0 °C for 1 h. The solvent was evaporated and dried under high vacuum. The residue was purified by dry-flash chromatography. Ethyl acetate–hexane (1/4) was used as a solvent for the purification. The product weight was 85 mg (0.24 mmol, 90% yield): δ 0.21 (TMS), 0.85 (s, $CH_3$), 2.04–2.89 (m, $CH_2$), 3.77 (s, $CH_3$), 4.53 (m, CH=C), 6.65–7.16 (m, Ar); TLC showed one spot ($R_f$ 0.75). Anal. C, H.

**Reaction of 3 with $CsSO_4F$.** Compound **3** (50 mg, 0.140 mmol) was dissolved in 3 mL of dry methylene chloride. The mixture was stirred at room temperature followed by addition of 105 mg (0.423 mmol) of $CsSO_4F$. The reaction mixture was stirred under $N_2$ for 17 h. At this time, 5 mL of dry $CH_2Cl_2$ was added, and the mixture was washed with 2 × 10-mL portions of water. The methylene chloride layer was separated, dried over anhydrous $MgSO_4$, and removed in vacuo. The residue was subjected to dry-flash chromatography to give 5–7 mg (0.019 mmol, 10–15% yield) of **5a** and **5b**.

The identities of **5a** and **5b** were confirmed by comparison of their $^1H$ and $^{19}F$ NMR data with known data reported by Katzenellenbogen et al.[1]

**Reaction of 3 with $XeF_2$.** In a 25-mL flask under $N_2$ atmosphere was placed 20 mg (0.056 mmol) of **3** in 3 mL of dry $CH_2Cl_2$ followed by addition of 30 mg (0.178 mmol) of $XeF_2$. The mixture was stirred at 25 °C for 30 min. After this time, dry $CH_2Cl_2$ (2 mL) was added, and the methylene chloride solution was washed with 2 × 5-mL portions of water. The organic layer was separated, dried over anhydrous $MgSO_4$, and removed in vacuo. The residue was subjected to flash chromatography to give 7.0 mg (0.022 mmol, 44% yield) of **5a**.

**Reaction of 3 with $F_2/N_2$.** To a well-stirred mixture of 90 mg (0.253 mmol) of **3** in 20 mL of freon at −78 °C was bubbled a mixture of 5–10% $F_2/N_2$. TLC analysis did not show any traces of the starting material after 5 min. Fluorine gas flow was shut off, and nitrogen gas was run into the solution for 1–2 more minutes. The solvent was removed on a rotary evaporator, and the residue was purified by flash chromatography to give 9–10 mg (0.031 mmol, 12% yield), mp 118–120 °C. The $^{19}F$ NMR spectrum shows that the aromatic ring has been fluorinated as well.

**Reaction of 3 with $CF_3OF$.** In a dry flask was dissolved 50 mg (0.140 mmol) of **3** in 8 mL of dry $CH_2Cl_2$. Fluoroxytrifluoromethane was bubbled into the mixture at 0 °C for approximately 5 min. To the reaction mixture was added 5 mL of dry $CH_2Cl_2$ followed by extraction with 2 × 10-mL portions of water. The organic layer was separated and dried over anhydrous $MgSO_4$. The solvent was removed, and the residue was purified by flash chromatography. The yield based on the NMR spectroscopy was determined to be 10–15%.

**Preparation of 4.** Into a 50-mL round-bottomed flask was dissolved 270 mg (1.00 mmol) of estrone in 15 mL of isopropenyl acetate, followed by addition of 1.0 mL of concentrated $H_2SO_4$. The mixture was refluxed for 2 h under nitrogen atmosphere. Approximately 5 mL of the solvent was collected and discarded. An additional 5 mL of isopropenyl acetate and 1.0 mL of $H_2SO_4$ were added, and the mixture was refluxed for 45 more minutes. Once again, 5 mL of the solvent was distilled off and discarded. Anhydrous ether (10 mL) was added, and ether solution was washed twice with water and then with 10 mL of ice-cold sodium bicarbonate solution and another time with water. Ether layer was separated, dried over anhydrous $MgSO_4$, and evaporated on a rotary evaporator. The residue was purified chromatographically on a silica gel column with 40% ethyl acetate–hexane as the solvent to give 150 mg (0.424 mmol, 42%, mp 149–150 °C [lit.[10] mp 145–149 °C]) of the product: $^1H$ NMR ($CDCl_3$) δ 0.98 (s, $CH_3$), 2.30 (s, $CH_3$), 2.40 (s, $CH_3$), 2.50–3.00 (m, $CH_2$), 5.54 (d, CH=COAC), 6.8–7.3 (m, Ar). TLC showed only one spot ($R_f$ 0.52).

**Reaction of 4 with $CsSO_4F$.** To a solution of 54 mg (0.154 mmol) of **4** in 3 mL of dry $CH_2Cl_2$, was added 88 mg (0.355 mmol) of $CsSO_3F$. The mixture was stirred, under nitrogen atmosphere, for 17 h at room temperature. After this time, 15 mL of dry $CH_2Cl_2$ was added, and the mixture was washed with 2 × 10-mL portions of water. The organic layer was separated, dried over anhydrous $MgSO_4$, and removed on a rotary evaporator. The residue was purified on a silica gel column with 40% ethyl acetate–hexane as the solvent. The product weight was 11 mg (0.033 mmol, 22% yield, mp 148–151 °C).

**Reaction of 4 with $XeF_2$.** To a mixture of 74 mg (0.210 mmol) of **4** in 3 mL of dry $CH_2Cl_2$ was added 54 mg (.320 mmol) of xenon difluoride. The mixture was stirred under dry atmosphere of $N_2$ for 17 h. TLC showed no traces of the starting material after this period of time. Dry methylene chloride (10 mL) was added, and the mixture was washed with 2 × 10-mL portions of water. The organic layer was separated and dried over anhydrous $MgSO_4$. The weight of the product was 69 mg (0.21 mmol, 99% yield, mp 149–153 °C).

**Reaction of 4 with $F_2/N_2$ (Method I).** In a 50-mL pear-shaped flask was dissolved 58 mg (0.164 mmol) of **4** in 3 mL of dry $CH_2Cl_2$, and the mixture was cooled in an ice bath to 0 °C. $F_2/N_2$ (5–10% $F_2$) gas was bubbled through the $CH_2Cl_2$ mixture for 5 min. Dry $CH_2Cl_2$ (5 mL) was added, and the mixture was washed with 2 × 5-mL portions of water. The organic layer was separated, dried over anhydrous $MgSO_4$, and was removed in vacuo. The residue was purified chromatographically to give 33 mg (0.094 mmol, 56% yield, mp 118–121 °C).

**Reaction of 4 with $F_2/N_2$ (Method II).** To a mixture of 75 mg (0.212 mmol) of **4** in 5 mL of dry $CH_2Cl_2$ at −78 °C was bubbled a mixture of $F_2/N_2$ (5–10% $F_2$). TLC showed no traces of the starting substrate after 2–3 min. Dry $CH_2Cl_2$ (10 mL) was added, and the mixture was washed twice with water. The methylene chloride layer was separated and dried over anhydrous $MgSO_4$. After evaporating the solvent on a rotary evaporator, the residue was subjected to flash chromatography to give 30 mg (40% yield, 0.086 mmol) of the product (mp 118–121 °C).

**Reaction of 4 with $CF_3OF$.** Compound **4** (41 mg, 0.116 mmol) was dissolved in 3 mL of dry $CH_2Cl_2$. The mixture was chilled to 0 °C and stirred for 5 min. $CF_3OF$ was bubbled into the reaction mixture for approximately 15 min. The TLC did not show any evidence of the starting material remaining in the reaction vessel. Dry $CH_2Cl_2$ (5 mL) was added, and the mixture was washed with water. The organic layer was separated, dried over anhydrous $MgSO_4$, and then removed in vacuo. The residue was subjected to flash chromatography, but all attempts to purify the product failed. The crude weight of the product was 25 mg (65% yield, 0.075 mmol).

**Acknowledgment.** This research was funded by the National Institutes of Health and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

**Registry No.** **3**, 115419-13-1; **4**, 20592-42-1; **5a**, 116005-36-8; **5b**, 2383-29-1; **6a**, 116051-28-6; **6b**, 2249-40-3; 3-methylestrone ether, 1624-62-0; estrone, 53-16-7.

(10) Leeds, N.; Fukushima, D. K.; Gallagher, T. F. *J. Org. Chem.* **1954**, *76*, 2947.

## Search for Nucleophilicity Effect on the Face Selectivity of Addition to a Sterically Unbiased Ketone[1]

M.-H. Lin, J. E. Silver, and W. J. le Noble*

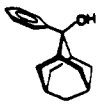
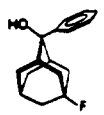
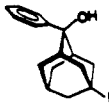
*Department of Chemistry, State University of New York, Stony Brook, New York 11794-3400*

*Received April 29, 1988*

In an earlier paper, we reported[2] the easily detectable face selectivity in the addition of nucleophiles to 5-sub-

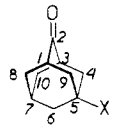
0022-3263/88/1953-5155$01.50/0 

Table I. Calculated[a] and Observed $^{13}C$ NMR Shifts

| | 1.3 | 2 | 4.9 | 5 | 6 | 7 | 8.10 |
|---|---|---|---|---|---|---|---|
|  | 31.447 | 35.827 | 42.708 | 92.570 | 42.708 | 31.447 | 35.827 |
|  | 35.482 | 75.436 | 32.850 | 26.847 | 37.592 | 27.359 | 34.760 |
|  | 38.005<br>38.527 | 74.218<br>73.469 | 39.228<br>41.641 | 92.110<br>91.527 | 42.655<br>42.506 | 29.924<br>29.892 | 31.139<br>30.883 |
|  | 39.780<br>38.527 | 74.092<br>73.469 | 37.675<br>39.731 | 91.967<br>91.015 | 42.556<br>42.506 | 30.361<br>30.404 | 33.179<br>32.793 |

[a] Underlined.

stituted adamantan-2-ones. Since there is virtually no steric bias in the approach to the carbonyl group, this selectivity must be electronic in nature. We furthermore



1-X

2

noted that this selectivity is for the syn face if X is electron withdrawing and for the anti face if it is a donor. This phenomenon can readily be explained on the basis of Cieplak's[3] hyperconjugative model of the transition state, in which it is assumed that delocalization of $\sigma$ electrons in the antiperiplanar bond into the incipient $\sigma^*$ orbital lowers the energy, and we subsequently showed that it is applicable to the capture of nucleophiles by carbocations and of electrophiles by olefins as well.[4] We use 1-F as the probe in many of our current studies since the fluorine-induced chemical shifts and C–F couplings allow for a more straightforward assignment of configuration of the two products obtained than with other 5-substituents.[5]

This interpretation allows but does not demand that the magnitude of the effect may be a function of the nature of the nucleophile, and accordingly, we searched for such an effect by the use of para-substituted phenyl Grignard reagents, with the substituent varying all the way from $CF_3$ to $NMe_2$. As is detailed below, no effect was found, and we were therefore surprised to learn from Gassman's recent paper[6] that in the alkylation of norbornen-7-one (**2**), a dramatic reversal in selectivity actually occurs when

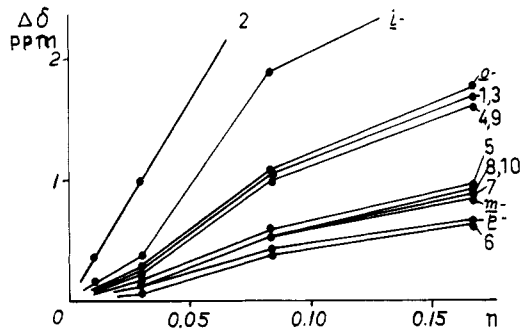



**Figure 1.**

methyl- and (pentafluoroethyl)lithium are compared. Such a reversal, should it occur in the 5-substituted adamantanones, is completely incompatible with the hyperconjugative model, and we therefore plunged into a study of Gassman's reagent with 1-F.

## Results and Discussion

Room-temperature addition of the phenyl Grignard reagents to 1-F led to mixtures of the two stereoisomeric (*E* and *Z*) cumyl alcohols in yields varying from 66% to 96%. The formation of the two isomeric alcohols was readily apparent from the $^{13}C$ NMR spectra of the crude mixtures; in each case, all seven resonances of the adamantane skeleton and the four benzene peaks of both isomers could be seen and identified as discussed below. In all cases, it proved possible to separate the products by means of flash chromatography, so that the pure isomers were available for characterization. The $^{13}C$ NMR spectra of all *E* isomers were very similar, as were those of the *Z* compounds, so that a detailed configurational study was necessary in only one instance. The products from the parent phenylmagnesium bromide were chosen for this purpose.

The key to the assignments of configuration was a study of the effect of the shift reagent $Eu(fod)_3$ on the $^{13}C$ NMR spectrum of the known 2-hydroxy-2-phenyladamantane.[7] In combination with the familiar chemical shift effects of bound oxygen, attached proton tests, and the intensities, the data of Figure 1 readily allowed unambiguous assignment of all carbon resonances. We then calculated the shifts to be expected for the two fluoro alcohols on the

(1) Based in part on the Ph.D. Thesis of M.-H.L.
(2) Cheung, C. K.; Tseng, L. T.; Lin, M.-H.; Srivastava, S.; le Noble, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 1598; **1987**, *109*, 7239.
(3) Cieplak, A. S. *J. Am. Chem. Soc.* **1981**, *103*, 4540.
(4) (a) Srivastava, S.; le Noble, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 5874. (b) Johnson, C. R.; Tait, B. D.; Cieplak, A. S. *J. Am. Chem. Soc.* **1987**, *109*, 5875.
(5) Srivastava, S.; Cheung, C. K.; le Noble, W. J. *Magn. Reson. Chem.* **1985**, *23*, 232.
(6) Gassman, P. G.; O'Reilly, N. J. *J. Org. Chem.* **1987**, *52*, 2481.
(7) Duddeck, H.; Hollowood, F.; Karim, A.; McKervey, M. A. *J. Chem. Soc., Perkin Trans. 2* **1979**, 360.

**Table II. Isomer Distribution in the Grignard Reactions with 5-Fluoroadamantan-2-one[a]**

| p-$XC_6H_4MgBr$ | Y,[b] % | E[c] alcohol, % | Z[c] alcohol, % |
|---|---|---|---|
| $Me_2N$ | 87 | 71 | 29 |
| MeO | 92 | 68 | 32 |
| Me | 86 | 70 | 30 |
| H | 96 | 72 | 28 |
| Br | 66 | 76 | 24 |
| $CF_3$ | 78 | 75 | 25 |

[a] In THF at room temperature. [b] Isolated. [c] By means of $^{13}C$ NMR; see text.

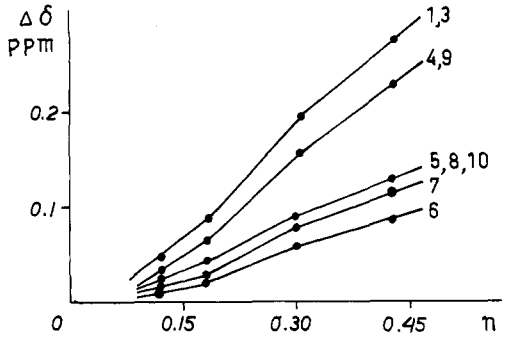


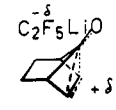

**Figure 2.**

basis of an additivity scheme that works very well with adamantane derivatives.[5] The two sets of calculated and observed resonances of the adamantane skeleton are compared in Table I; the agreement is clear and the assignment is unambiguous. All six of the epimeric alcohols were analyzed in this same way (the shift reagent study was done only with the parent compound). Our ratio measurements of the crude mixtures were based on integrations of the well-separated and unsplit $^{13}C_2$ peaks. The results are given in Table II.

The data show the previously noted tendency that all nucleophiles approach from the direction antiperiplanar to the electron richest bond. A clear trend within the series cannot be seen, however. If a linear correlation with $\sigma$ constants is assumed, the value $\Delta\rho \approx 0.1$, but one could with nearly equal justice say that all $E/Z$ ratios are equal at $2.6 \pm 0.4$.

The experiments with (perfluoroethyl)lithium were carried out basically as Gassman reported.[6] The assignments of the $^{13}C$ NMR resonances were based on the effects of $Eu(fod)_3$ on the parent alcohol (Figure 2), calculated and observed chemical shifts in the two isomers, attached proton tests, and fluorine couplings; the methylene–fluorine coupling with the nearby (through-space) adamantyl methylene carbons provided a helpful confirmation of our assignment. The analysis was based on both GC and $^{19}F$ NMR; a sample of pure $E$ isomer was obtained by partial crystallization of the crude mixture. The result is that this nucleophile approaches from the syn direction to produce primarily the $E$ alcohol; its preference is about 3:1, comparable to that of methyllithium[2] (7:3). Thus, the remarkable turnaround seen by Gassman with **2** does not occur with our probe. His conclusion that the nature of the nucleophile affects face selectivity must therefore be seen in the context of a special case.

Clark and Warkentin[8] had noticed earlier that vinyl- and phenyllithium also preferred the anti face of **2**, and they considered the possibility that anti approach to this ketone may occur if a sufficiently free lithium cation can strongly coordinate with the oxygen, promoting bridging of the carbonyl carbon to the double bond. While these authors considered "quite unlikely" that such nucleophiles could be "capable of inducing non-classical character into the ketone", our own recent work in this area[2] has shown that hyperconjugative effects operate very similarly in ketone alkylations and in the capture of carbocations. It is now obvious that the double bond plays a special role in the case of **2**, and we feel that Warkentin's ion-pair representation **3** is probably the correct explanation. The formation of tricyclo[3.2.0.0$^{4,6}$]hept-2-ene (**4**) in the lithium aluminum hydride reduction of 7-chloronorbornadiene has also been ascribed to double-bond involvement.[9]

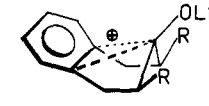



**3**

**4**

It is clear from these results that one should be very careful in drawing conclusions concerning face selectivity from studies using probes in which one or both faces have an unsaturated system in a position to participate. The $\pi$ bond or benzo ring may not serve merely as a space label but catalyze one of the two possible reactions in such instances. A case in point is the recent observation that 4-benzocyclohepten-1-ones **5** are reduced preferably at the equatorial side; it was concluded that Cieplak's model of the transition state is incorrect.[10] Since structure **6** does not seem to have been considered as the possible cause of this result, we feel that the conclusion does not rest on an experimentally sound basis.


**5**




**6**

Indeed, we identify an additional reason why probes–including the 5-substituted adamantanes–must be used with circumspection. Many studies employ reactions that involve metal ions capable of coordinating with covalently bound halogen: chelation may then affect the results. Our synthesis of the (*E*)- and (*Z*)-5-deuterioadamantan-2-ols from the corresponding 5-bromoadamant-2-yl trimethylsilyl ethers is in fact based on the apparently facile coordination of oxygen atom with the metal ion in the reducing agent, zinc borohydride (deuteride).[11] We have noted another instance of this effect in the present study: if the product $E/Z$ mixture of 5-fluoro-2-phenyladamantan-2-ols in the Grignard reaction is exposed to the phenylmagnesium bromide for a long time or at elevated temperatures, halogen exchange sets in with a strong preference for the $Z$ alcohol, thus giving artificially high $E/Z$ ratios of fluoro alcohol.

Although there is thus at present little hard information available that clearly shows nucleophilicity effects on face selectivity in sterically unbiased ketones, such effects must not yet be ruled out. Thus, we consistently find that hydride reductions have somewhat smaller preferences for approach syn to an electronegative 5-substituent then do lithiations, Grignard reactions, and ethynylations. Para substituents *do* affect syn/anti ratios in the reaction of phenyl Grignard reagents with norbornenone,[12,13] and re-

(8) Clark, F. R. S.; Warkentin, J. *Can. J. Chem.* **1971**, *49*, 2223.

(9) Story, P. R. *J. Am. Chem. Soc.* **1961**, *83*, 3347.

(10) Mukherjee, D.; Wu, Y.-D.; Fronczek, F. R.; Houk, K. N. *J. Am. Chem. Soc.* **1988**, *110*, 3328.

(11) Lin, M.-H.; le Noble, W. J. *J. Label. Comp. Radiopharm.* **1986**, *24*, 1285.

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.

**Acknowledgment.** We thank Dr. C.-K. Cheung for his assistance with one experiment. The work reported herein was supported by the National Science Foundation (Grant Che8605068) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. W. le N. thanks the Japanese Ministry of Education, Science and Culture (Mombusho) for supporting his stay at the University of Oita. We thank Professor Paul G. Gassman for making unpublished data from his laboratory available to us.

**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.

(12) Fentiman, A. Ph.D. Thesis, Ohio State University.
(13) Gassman, P. G.; Schaffhausen, J. G.; Raynolds, P. W. *J. Am. Chem. Soc.* **1982**, *104*, 6408.

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

Anita Vasudevan and Gerald F. Koser*

*Department of Chemistry, The University of Akron, Akron, Ohio 44325*

*Received April 29, 1988*

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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