filtered off. Removal of the solvent in vacuo left 4.49 g of an oil.

A sample (0.5 g) was taken up in THF (15 mL) and added to 10% HCl (20 mL). The resulting bright yellow mixture was extracted with pentane (4 × 5 mL) and the yield of 2,3-heptanedione was quantitated by gas chromatography (0.05 g). The pentane extract was then concentrated and the oil purified by preparative thin-layer chromatography (20 cm × 20 cm × 2000 μm, silica gel; 20% ether in petroleum ether), and 0.370 g of *N*-3-(2-oxoheptyl)-*N*-phenyltriflamide was isolated. The conversion from 3-bromo-2-heptanone was 23% to the anil and 64.4% to the substitution product or 87.4% overall. *N*-3-(2-Oxoheptyl)-*N*-phenyltriflamide was recrystallized from hexane: mp 55.5–58.5 °C; IR (KBr) 2961, 2938, 1722, 1361, 1224, 1210, 1185, 1145 cm^{-1}; NMR ($CDCl_3$) δ 7.30 (s, 5), 4.70 (t, 1, J = 7.4 Hz), 2.29 (s, 3), 1.39 (m, 6), 0.87 (t, 3, J = 5.2 Hz); mass spectrum, m/e (rel intensity) 337 (10), 294 (80), 161 (12), 132 (6), 120 (10), 119 (100), 118 (9), 104 (7), 77 (15). Anal. Calcd for $C_{14}H_{18}F_3NO_3S$: C, 49.84; H, 5.84. Found: C, 49.96; H, 5.45.

The product mixture (2.3 g) was refluxed in 25 mL of THF with potassium carbonate (0.7 g, 0.005 mol). After 18 h, GC/MS showed complete loss of the initial alkylation product with only elimination product remaining. An excess of ethylenediamine (0.82 g, 0.014 mol) was added and the mixture heated under reflux for 60 h. Gas chromatographic/mass spectroscopic analysis indicated aniline and the dihydropyrazine. This mixture was added to a solution of methanol saturated with sodium hydroxide. The solution was kept between 60 and 70 °C, and oxygen was added beneath the surface of the reaction throughout the 1.5 h required for the addition and the additional hour of heating. The reaction mixture was poured into water and extracted with pentane. The extracts were back-extracted with 5% HCl and a saturated salt solution and dried (Na_2SO_4). Concentration of the extracts followed by preparative GC produced the pyrazine in 65% yield. IR and mass spectra are identical with those previously described,[15] and the NMR spectrum is consistent with the structure: NMR ($CDCl_3$) δ 8.27 (s, 2), 2.82 (t, 2, J = 7.6 Hz), 2.57 (s, 3), 1.60 (m, 4), 0.95 (t, 3, J = 6.0 Hz).

Registry No. 2-Isobutyl-3-methylpyrazine, 13925-06-9; 2-methyl-3-phenylpyrazine, 29444-53-9; 2-methyl-3-octylpyrazine, 71700-39-5; 2-*n*-butyl-3-methylpyrazine, 15987-00-5; *N*-[3-(5-methyl-2-oxohexyl)]-*N*-phenyltriflamide, 71700-40-8; *N*-[3-(3-phenyl-2-oxopropyl)]-*N*-phenyltriflamide, 71700-41-9; *N*-[3-(2-oxoheptyl)]-*N*-phenyltriflamide, 71700-42-0; *N*-[3-(2-oxoheptyl)]aniline, 71700-43-1; 5-methyl-3-bromo-2-hexanone, 71700-44-2; 3-bromo-3-phenyl-2-propanone, 23022-83-5; 3-bromo-2-undecanone, 71700-45-3; 3-bromo-2-heptanone, 51134-59-9; *N*-phenyltriflamide, 456-64-4; ethylenediamine, 107-15-3.

(15) P. Fridel, V. Krampl, T. Radford, J. Renner, F. Shepard, and M. Granturco, *J. Agric. Food Chem.*, **19**, 530 (1971).

Application of *N*-Phenyltriflamide to the Synthesis of Deoxyaspergillic Acid

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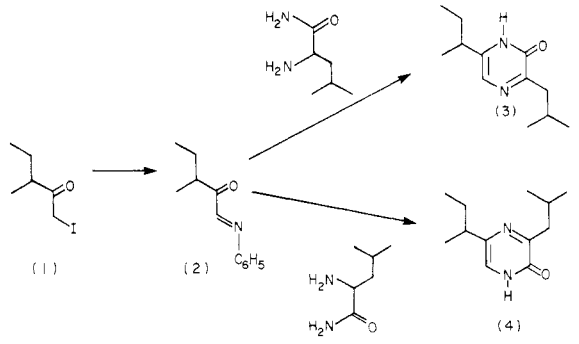
Received June 26, 1979

Because of its structural relationship to aspergillic acid, deoxyaspergillic acid (**3**, Scheme I) has long been of interest to both organic chemists and biochemists.[2-4] This 3,6-disubstituted 2-pyrazinone is a naturally occurring secondary metabolite produced by certain species of aspergillis[5] and streptomyces.[6,7] Early workers determined that when aspergillic acid was reduced with hydrazine, a single product, deoxyaspergillic acid, resulted.[2] In this paper, we focus on the development of an abbreviated synthesis of deoxyaspergillic acid employing the unique properties of *N*-phenyltriflamide in the preparation of the key intermediate, a primary α-imino ketone.[8-10] This investigation demonstrates not only the general utility of our recently developed pyrazine synthesis[8] but also the regioselectivity in the condensation of an α-keto amine with leucinamide.

Scheme I. Two Possible Condensation Modes[a] of α-Imino Ketone 2 with Leucinamide



[a] Even though both modes are possible, only deoxyaspergillic acid (3) was observed.

The synthetic concept is based on our earlier observation that imino ketones generated in situ from *N*-phenyltriflamide and the appropriate α-halo ketone can be smoothly condensed with 1,2-diamines to produce pyrazines.[8] The initial investigation focused on the condensation of symmetrical diamines with imino ketones while the present study is aimed at the regiospecific condensation of two unsymmetrical synthons, a keto imine (**2**) and leucinamide. Clearly, the leucinamide can add in two different directions to the imino ketone generating either the desired product (**3**) or compound **4** (Scheme I).

A review of the pertinent literature on pyrazinone syntheses revealed that early workers[11,12] found only the 3,5 isomers when condensing unsymmetrical dicarbonyls with α-aminoamides. However, recent workers[13] found that the product of the condensation of leucinamide and methylglyoxal was 33% 2-pyrazinone. Although the majority of the product was still 3,5 isomer, this encouraged us to consider the application of our pyrazine synthesis to the synthesis of deoxyaspergillic acid. Our imino ketone offered the additional advantage of two electrophilic centers with substantially different electronic properties.

The halo ketone (**1**) required for the synthesis of the

(1) This research was done in partial fulfillment of the requirements for a Ph.D. degree at the University of Maryland, College Park, MD.

(2) G. T. Newbold, W. Sharp, F. Spring, *J. Chem. Soc.*, 2679 (1951).

(3) J. J. Gallagher, G. T. Newbold, W. Sharp, and F. S. Spring, *J. Chem. Soc.*, 4870 (1952).

(4) Y. Chigira, M. Masaki, and M. Ohta, *Bull. Chem. Soc. Jpn.*, **39**, 1014 (1966).

(5) T. Yokotsuka, M. Sasaki, T. Kikuchi, Y. Asao, and A. Nobuhara, "Biochemistry of Some Foodborne Microbial Toxins", R. I. Matiles and G. N. Wogan, Eds., MIT Press, Cambridge, MA, 1967, p 131.

(6) K. Tatsuka, T. Tsuchiya, and S. Umeyawa, *J. Antibiot.*, **25**, 674 (1972).

(7) K. Tatsuka, K. Fujimoto, M. Yamashita, T. Tsuchiya, S. Umeyawa, and H. Umeyawa, *J. Antibiot.*, **26**, 606 (1973).

(8) R. J. Bergeron and P. G. Hoffman, *J. Org. Chem.*, preceding paper in this issue.

(9) J. B. Hendrickson, D. D. Sternbach, and K. W. Bair, *Acc. Chem. Res.*, **10**, 306 (1977).

(10) R. J. Bergeron and P. G. Hoffman, *J. Org. Chem.*, **44**, 1835 (1979).

(11) R. G. Jones, *J. Am. Chem. Soc.*, **71**, 78 (1949).

(12) G. Karmas and P. E. Spoerri, *J. Am. Chem. Soc.*, **74**, 1580 (1952).

(13) R. M. Seifert, R. G. Buttery, D. G. Guadagni, D. R. Black, and J. G. Harris, *J. Agric. Food Chem.*, **20**, 135 (1972).

0022-3263/80/1945-0163$01.00/0

α-keto imine was generated from commercially available 3-methyl-1-pentene by reaction with $AgCrO_4/I_2/C_5H_5N$.[14] This reaction resulted in a 3.5:1 mixture of the primary iodo ketone and the primary iodo alcohol in addition to a small amount of 2-iodo-3-methylpentanal. The iodo ketone (1) was purified by either column or preparative thin-layer chromatography and when reacted with anilinetriflamide in THF in the presence of K_2CO_3, produced the expected keto imine (2). However, if desired, the reaction of the iodo ketone with anilinetriflamide could be stopped at the substitution product by using acetone and only 0.5 equiv of base.[9]

Initial attempts to condense the keto imine (2) with leucinamide in methanol–water at 10 and 40 °C following previously reported procedures for condensation of leucinamide hydrochloride with dicarbonyl compounds gave only 8.4 and 9.2% yields of the desired compound (3), respectively (Scheme I). Because of the potential sensitivity of the reactants to solvolysis it seemed likely that methanol and water used in the condensations were interfering with this seqence.[15] The remainder of the reactions were run in anhydrous THF by adding the anil directly to the free amino amide and piperidine. Two reactions, one run at −40 °C and one at reflux, gave 43.4 and 54.0% yield, respectively, of the 3-isobutyl-6-*sec*-butyl-2-pyrazinone (3). The physical and spectroscopic properties of this product were identical with those previously reported for deoxyaspergillic acid.[4,16,17] We were unable to identify any other pyrazines.

Experimental Section

All melting points and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 257 or 299B spectrophotometer. Proton NMR spectra were determined with a Varian EM360. Chemical shifts are reported in parts per million with tetramethysilane as an internal standard. Mass spectra were obtained on a Du Pont 21-490 by using direct injection or by scanning the gas chromatographic effluent. Gas chromatographic analyses were obtained with either a Varian 1400 equipped with a flame-ionization detector and 5 ft × 6 mm o.d. glass column packed with 10% SE30 on Chromosorb WAW DMCS or a Hewlett-Packard 5710 equipped with a thermal-conductivity detector and a 6 ft × 6 mm o.d. glass column packed with 5% SF96 on Chromosorb WAW DMCS. Preparative gas chromatography was done on the latter instrument or on a Varian 90P equipped with a thermal conductivity detector and a $^1/_4$ in. × 8 ft steel column packed with 10% SF96. Preparative thin-layer plates were supplied by Analtech, Inc. Microanalyses were done by Dr. F. Kasler at the University of Maryland or Galbraith Laboratories, Knoxville, TN.

Oxidation of 3-Methyl-1-pentene (Synthesis of 1-Iodo-3-methyl-2-pentanone). The preparation of the reagent Ag_2CrO_4 and the oxidation of 3-methyl-1-pentene (5.8 g, 67 mmol) were carried out according to the procedure of Cardillo and Shimizu[14] with the exception that when the reaction was completed, the filtered CH_2Cl_2 solution was concentrated to half its volume and diluted with pentane. This modification removed more salts and eliminated the emulsion which formed during the $Na_2S_2O_3$ wash. A crude dark liquid product (11.5 g) was isolated. Gas chromatographic analysis and comparison with authentic samples showed this to be 71.7% 1-iodo-3-methyl-2-pentanone and 21.4% 1-iodo-3-methyl-2-pentanol. In addition, a small amount of 2-iodo-3-methylpentanal was identified by its mass spectrum obtained from the effluent of the gas chromatographic column. Although the crude product could be distilled, bp 44.5–47.5 °C (0.4 mmHg), the desired iodo ketone was still somewhat contaminated. A clean separation could be achieved by column chromatography using silica gel, eluting with hexane with increasingly greater concentrations of ether, or by preparative thin-layer chromatography on a 20 × 20 cm, 2000 μm silica gel plate, eluting with 9:1 hexane:ether. The area containing the α-iodo aldehyde darkened rapidly, and this byproduct, when eluted from the silica gel and concentrated, was recovered as a dark oil which quickly became viscous and then tarry. The yield of 1-iodo-3-methyl-2-pentanone based on the olefin was 54.4% while the iodo alcohol was 16.1%.

2-Iodo-3-methylpentanal: mass spectrum (70 eV), *m/e* (rel intensity) 226 (≪1), 99 (27), 81 (15), 55 (24), 43 (100), 39 (20), 29 (23).

1-Iodo-3-methyl-2-pentanol: NMR ($CDCl_3$) δ 3.38 (m, 3), 2.18 (s, 1, D_2O exchangeable), 1.52 (m, 3), 0.98 (m, 6); IR (neat) 3380, 2965, 1456, 1375 cm^{-1}; mass spectrum (70 eV), *m/e* (rel intensity) 228 (3), 171 (35), 101 (45), 83 (53), 57 (100), 55 (22), 45 (53), 43 (25), 41 (57), 29 (43). Anal. Calcd for $C_6H_{13}IO$: C, 31.60; H, 5.75. Found: C, 31.64; H, 5.83.

1-Iodo-3-methyl-2-pentanone: NMR ($CDCl_3$) δ 3.90 (s, 2), 2.92 (m, 1), 1.61 (m, 2), 1.18 (d, 3, J = 6.6 Hz), 0.91 (t, 3, J = 6.6 Hz); IR (neat) 2967, 1701, 1457, 1409, 1376, 1179, 1140, 1023 cm^{-1}; mass spectrum (70 eV), *m/e* (rel intensity) 226 (6), 85 (66), 57 (100), 43 (16), 41 (65). Anal. Calcd for $C_6H_{11}IO$: C, 31.88; H, 4.90. Found: C, 32.04; H, 4.96.

***N*-Phenyl-*N*-(3-methyl-2-oxo-1-pentyl)triflamide.** Previous experience with primary halo ketones had indicated that these additions require less than 1 equiv of potassium carbonate. This prevented further reaction. Therefore, 1-iodo-3-methyl-2-pentanone (1.03 g, 4.5 mmol), *N*-phenyltriflamide (1.00 g, 4.5 mmol), and K_2CO_3 (0.3 g, 2.2 mmol) were combined and refluxed in 50 mL of acetone for 6 h. The solution was decanted from the salts and concentrated to a pasty solid. This was stirred in CH_2Cl_2, the precipitated KSO_2CF_3 and KI were filtered off, and the filtrate was concentrated to an oily product (1.39 g, 95.8% yield). This could be further purified, if desired, by preparative thin-layer chromatography on a 20 × 20 cm, 2000 μm silica gel plate, eluting with 15% ether in petroleum ether, to give a lighter yellow oil: NMR ($CDCl_3$) δ 7.43 (m, 5), 4.62 (s, 2), 2.48 (m, 1), 1.42 (m, 2), 1.01 (d, 3, J = 7.0 Hz), 0.77 (t, 3, J = 7.0 Hz); IR (neat) 2972, 1735, 1596, 1493, 1390, 1228, 1148, 1458, 877, 692 cm^{-1}; mass spectrum (70 eV), *m/e* (rel intensity) 323 (4), 106 (35), 105 (39), 85 (35), 77 (15), 57 (100). Anal. Calcd for $C_{13}H_{16}F_3NO_3S$: C, 48.29; H, 4.99; N, 4.33. Found: C, 48.32; H, 4.97; N, 4.51.

Conversion of 1-Iodo-3-methyl-2-pentanone Directly to the α-Imino Ketone. The iodo ketone (0.9 g, 4.0 mmol), *N*-phenyltriflamide (1.05 g, 4.6 mmol), and K_2CO_3 (1.43 g, 10.3 mmol) in 100 mL of THF (LAH) were refluxed for 48 h. The only product identified by its mass spectrum was the desired primary imino ketone: mass spectrum (70 eV), *m/e* (rel intensity) 189 (3), 133 (10), 105 (10), 104 (100), 77 (42). This material, when isolated, discolored, and its NMR and IR spectra were not clearly interpretable; however, the NMR spectrum did show the significant absences of the methylene protons at δ 4.62 found in the substitution product and δ 3.90 in the iodo ketone.

One-fourth of the above reaction mixture (1.0 mmol) was added to a solution of leucinamide (0.12 g, 0.9 mmol) and piperidine (0.085 g, 1.0 mmol) in 25 mL of tetrahydrofuran and the reaction refluxed for 24 h. The reaction was cooled and concentrated to a pasty yellow solid which was stirred with 5% HCl and ether at ice-bath temperature. The ether layer was removed and the acid layer saturated with salt and extracted with ether. All the organic extracts were combined and washed with a saturated salt solution. The ether was concentrated and the wet residue dried in methylene chloride (Na_2SO_4). The yellow solid recovered on solvent removal was purified by preparative thin-layer chromatography on a 20 × 20 cm, 2000 μm silica gel plate, eluting with 3:2 ether–petroleum ether, to give 101 mg of deoxyaspergillic acid (54% yield based on the amino amide). This was recrystallized from ethanol–water: mp 98.5–100.5 °C (lit.[4] mp 99.5–100.5 °C); IR identical with that given by Nakamura;[16] NMR identical with that reported by MacDonald;[17] the mass spectrum is consistent with the proposed structure (70 eV), *m/e* (rel intensity) 208 (13), 193 (28), 167 (11), 166 (100), 137 (91), 41 (13).

Acknowledgment. The authors wish to thank McCormick and Co., Inc., Hunt Valley, MD, for their

(14) G. Cardillo and M. Shimizu, *J. Org. Chem.*, **42**, 4268 (1977).
(15) T. Konakahara and Y. Takagi, *Heterocycles*, **9**, 1733 (1978).
(16) S. Nakamura, *Agric. Biol. Chem.*, **25**, 658 (1961).
(17) J. C. MacDonald, G. G. Bishop, and M. Mazurek, *Tetrahedron*, **32**, 655 (1976).

generous support of this research.

Registry No. 1, 71886-29-8; 2, 71886-30-1; 3, 21641-71-4; 3-methyl-1-pentene, 760-20-3; 2-iodo-3-methylpentanal, 71886-31-2; 1-iodo-3-methyl-2-pentanol, 71886-32-3; *N*-phenyl-*N*-(3-methyl-2-oxo-1-pentyl)triflamide, 71901-58-1; *N*-phenyltriflamide, 456-64-4; leucinamide, 13366-40-0.

Reactions of Nitrosonium Tetrafluoroborate in Acetonitrile with Organic Molecules Containing Nonbonding Electrons. Synthesis of Acetamides

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Received June 25, 1979

We have recently found that NO_2BF_4 in acetonitrile will abstract hydrogen from saturated hydrocarbons. Under these relatively mild reaction conditions, the incipient carbenium ion is efficiently trapped by the nitrile solvent, and upon hydrolysis of the resulting nitrilium ion acetamides are produced in good yield.[1a] The Lewis acid character of the nitronium (NO_2^+) ion is also manifested in its complexation with the nonbonding (n) electrons of alkyl halides[1b] and ethers, inducing C–X bond heterolysis which results in acetamide formation (eq 1).[1c] Hydrogen,

$$R_3CX + NO_2BF_4 \xrightarrow{CH_3CN} R_3C\text{-}N^+{\equiv}CCH_3 + NO_2X \quad (1)$$

$$\downarrow H_2O$$

$$R_3CNCCH_3 \quad (\mathrm{HO},\ \mathrm{O})$$

halogen, and alkoxide transfer to the nitronium ion was also observed with $CF_3C(O)ONO_2$ in trifluoroacetic acid and $CH_3C(O)ONO_2$ in acetic acid, affording alkyl trifluoroacetates and alkyl acetates, respectively.[1d] We now report a comparable series of reactions with $NOBF_4$ as the electrophilic reagent in acetonitrile.

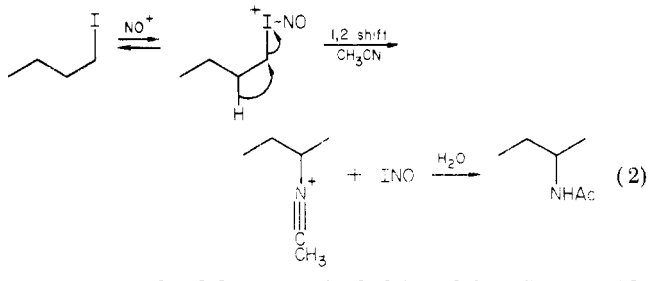
The nitrosonium ion, NO^+, is a reactive electrophilic species that has been utilized synthetically with alkenes,[2] amines,[3] amides,[4] sulfoxides,[5] and activated aromatic compounds.[6] Nitrosonium salts, with nonnucleophilic ions like $NOBF_4$ and $NOPF_6$, can be used to advantage in diazonium ion preparation from aryl or primary amines[7] and in the nitrosative decomposition of aliphatic azides.[8] Amides and sulfonamides were found to react with $NOBF_4$ under mild conditions to give the corresponding acids.[4] This versatile electrophilic reagent has been shown to abstract hydride ion from activated benzylic positions,[9a] to oxidize benzyl alcohols, and to oxidize trimethylsilyl and tributylstannyl ethers to carbonyl compounds.[9b] Activated benzyl and benzhydryl esters are also oxidatively cleaved to the parent acid or ketone.[9c] Alkenes also undergo electrophilic addition by $NOBF_4$ in acetonitrile to afford 2-methyl-*N*-hydroxyimidazolium salts.[9d]

Results and Discussion

To date there has been no systematic study of the reaction of $NOBF_4$ with alkyl halides or ethers in the condensed phase. In the gas phase, ion–molecule reactions of NO^+ with organic halides[10] closely paralleled our results with both NO^+ and NO_2^+ in solution.[9] In the absence of solvent, NO^+ exhibits a high electron affinity and will abstract hydrogen from normal, branched, or cyclic hydrocarbons.[10,11] It was the goal of the present study to provide a comparison between the reactivity of NO_2BF4 and $NOBF_4$ in acetonitrile and to develop a convenient synthetic procedure for the conversion of alkyl halides and ethers to their respective acetamides.

In a typical reaction, the alkyl halide or ether is added to 1 equiv of $NOBF_4$ in acetonitrile at 0 °C and allowed to stir at room temperature; the reaction is then quenched with water. Product isolation is not complicated by the formation of side products which give difficult separation problems. The results given in Table I serve to define the scope and utility of this new procedure.

The reactivity of $NOBF_4$ toward alkyl iodides was very similar to that observed with NO_2BF_4/CH_3CN. Both tertiary and secondary alkyl iodides reacted smoothly with $NOBF_4$ to afford their acetamides. As anticipated on the basis of relative carbenium ion stability, *n*-butyl iodide reacted slowly and gave equal amounts of 1-butyl- and 2-butylacetamides. The latter product arises from a 1,2 hydride shift to the developing adjacent positive center (eq 2).[12] The selective reaction of only one functional



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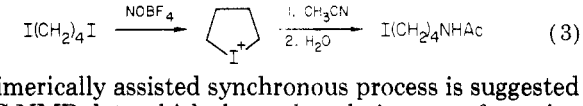
group in 1,4-diiodobutane afforded (4-iodobutyl)acetamide. The absence of rearranged product is most likely a result of neighboring-group participation by iodine (eq 3). An



(3)

anchimerically assisted synchronous process is suggested by ^{13}C NMR data which shows the relative rate of reaction of 1,4-diiodobutane to be at least 10 times greater than that of 1-iodobutane.

The reaction times for the secondary halides were typically longer (24 h) with $NOBF_4$ than with NO_2BF_4. 1-Bromopropane and 1-bromooctane were unreactive toward

(1) (a) Bach, R. D.; Holubka, J. W.; Badger, R. C.; Rajan, S. J. *J. Am. Chem. Soc.* **1979**, *101*, 4416. (b) Bach, R. D.; Holubka, J. W.; Taaffee, T. H. *J. Org. Chem.* **1979**, *44*, 35. (c) *ibid.* **1979**, *44*, 1739. (d) Bach, R. D.; Taaffee, T. H., *J. Org. Chem.*, in press.

(2) Beckham, L. J.; Fessler, W. A.; Kise, M. A. *Chem. Rev.* **1951**, *48*, 319. Ohno, M.; Naruse, N.; Torimitsu, S.; Teresawa, I. *J. Am. Chem. Soc.* **1966**, *88*, 3168.

(3) Sigel, H.; Brintzinger, H. *Helv. Chim. Acta* **1965**, *48*, 433. France, H.; Heilbron, I. M.; Hey, D. H. *J. Chem. Soc.* **1940**, 369. Skinner, W. A.; Gram, H. F.; Baker, B. R. *J. Org. Chem.* **1960**, *25*, 777.

(4) Olah, G. A.; Olah, J. A. *J. Org. Chem.* **1965**, *30*, 2386.

(5) Loeppky, R. N.; Chang, D. C. K. *Tetrahedron Lett.* **1968**, 5415.

(6) Allan, Z. J.; Podstata, J.; Snobl, D.; Jarkovsky, J. *Tetrahedron Lett.* **1965**, 3565.

(7) Rutherford, K. G.; Redmond, W.; Rigamonti, J. *J. Org. Chem.* **1961**, *26*, 5149.

(8) Doyle, M. P.; Whitefleet, J. L.; Bosch, R. J. *J. Org. Chem.* **1979**, *44*, 2923.

(9) (a) Olah, G. A.; Salem, G.; Staral, J. S.; Ho, T.-L. *J. Org. Chem.* **1978**, *43*, 173. (b) Olah, G. A.; Ho, T.-L. *Synthesis* **1976**, 609. (c) *Ibid.* **1977**, 418. (d) Scheinbaum, M. L.; Dines M. B. *Tetrahedron Lett.* **1971**, 2205.

(10) Williamson, A. D.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 5714.

(11) Searles, S. K.; Sieck, L. W. *J. Chem. Phys.* **1970**, *53*, 794.

(12) It is doubtful that primary and secondary substrates involve discrete carbenium ions. Optically active 2-bromo- and 2-methoxyoctane react with NO_2BF_4 to provide 2-acetamides with net inversion of configuration.

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