and fluorohydrin[15] derivatives. Since these latter compounds can also be prepared with the aid of acetyl hypofluorite this reagent seems to be quite versatile and useful in organic chemistry. What is more, unlike the characteristic syn addition reactions of AcOF to double bonds, this work opens a way for the anti addition of the elements of fluorine and oxygen across olefins. Last, but not least, is the possibility of introducing the ^{18}F radioisotope by using the relatively easily labeled $AcO^{18}F$,[1d] and since the reactions described above are quite fast, this method could be very useful for preparation of fluoro ethers suitable for positron emitting tomography.

Experimental Section

^1H NMR spectra were recorded with a Bruker WH-90 and a Bruker WH-360 spectrometers at 90 and 360 MHz, respectively, with $CDCl_3$ as a solvent and Me_4Si as an internal standard. The ^{19}F spectra were measured at 84.67 and 338.8 MHz, respectively, and are reported in parts per million upfield from $CFCl_3$, which also served as internal standard. Mass spectra were measured with a Du Pont 21-491B spectrometer. IR spectra were recorded as neat films, in $CHCl_3$ solution or in KBr pellets on a Perkin-Elmer 177 spectrometer.

Preparation of the Mercury Derivatives. The appropriate olefin (10% excess) and $Hg(OAc)_2$ were mixed in MeOH at room temperature until no more precipitation of HgO occurred when NaOH was added. A saturated NaCl solution was then added, and the solid was filtered and recrystallized from MeOH.[4]

General Fluorination Procedure. A description of the setup and the procedure for working with elemental fluorine have previously been described.[14] It is worth repeating that F_2 and AcOF should be treated with care since they are strong oxidizers. The work should be conducted in an efficient hood or in a well-ventilated area. The toxicity of AcOF is not yet known, but some fluoroxy reagents are suspected to be strong poisons. If elementary precautions are taken, work with fluorine and its derivatives is safe and relatively simple.

Preparation of AcOF and methods of reaction were described in our work dealing with aromatic fluorinations.[1b] Two methods of addition were used. Method A consists of the addition of a cold $CHCl_3$ solution of the olefin to the AcOF solution, while in method B the oxidizing solution of AcOF was added dropwise with the aid of a pipet to the cold alkene solution so that the progress of the reaction could be monitored. In general the latter method resulted in a cleaner products. The reactions were usually carried out on scales of 10–40 mmol using 1.5–3 fold excess of AcOF, and, unless otherwise stated, the conversions were higher than 95%. The term "worked up as usual" means stopping the reaction by pouring it into 500 mL of water, washing the organic layer with $NaHCO_3$ solution followed by water until neutral, drying the organic layer over $MgSO_4$, and finally evaporating the solvent. The crude product was usually purified by vacuum flash chromatography using silica gel 60-H (Merck) and if needed also by HPLC (Waters) on Merck's LiChrosorb Si-100. Unless a melting point is given, the products are liquids.

Fluorination of 1 was carried out according to method A using 10 mmol of the mercury derivative and 20 mmol of AcOF at −78 °C. After 5 min, the reaction being complete and worked up as usual was flash chromatographed by using 5% EtOAc in petroleum ether as eluent. *trans*-2-Fluoro-1-methoxycyclohexane (**2**)[5] was thus isolated as an oil in 90% yield: NMR δ 4.30 (1 H, dm, J = 51 Hz, $W_{h/2}$ = 30 Hz), 3.41 (3 H, s); ^{19}F NMR −188.4 ppm (br d, J = 51 Hz).

Fluorination of 3 was carried out on 10 mmol at room temperature according to method B using 15 mmol of AcOF. The crude reaction mixture was flash chromatographed by using 5% EtOAc in petroleum ether as eluent. The fluoro ether **4** was thus isolated as an oil in 90% yield: NMR δ 4.64 (1 H, dm, J = 48 Hz), 3.50 (1 H, m), 3.42 (3 H, s), 2.2–1.2 (12 H, m); ^{19}F NMR −168.7 ppm (m). Anal. Calcd for $C_9H_{17}FO$: C, 67.50; H, 10.62. Found: C, 67.38; H, 10.49.

Fluorination of 5 was carried out on 10 mmol at 0 °C according to method B using 15 mmol of AcOF. The crude reaction mixture was flashed chromatographed by using 5% EtOAc in petroleum ether as eluent. The fluoro ether **6**[6] was thus isolated as an oil in 80% yield: NMR δ 7.35 (4 H, m), 5.90 (1 H, dd, J_1 = 57 Hz, J_2 = 4 Hz), 4.29 (1 H, m), 3.50 (3 H, s), 2.92 (2 H, m); ^{19}F NMR −178.0 ppm (dd, J_1 = 57 Hz, J_2 = 4 Hz).

Fluorination of 7 was carried out on 8 mmol according to method A using 30 mmol of AcOF. No reaction took place at −78 °C, but the starting material was fully consumed when the reaction mixture was allowed to warm up to 0 °C. After flash chromatography using 10% EtOAc in petroleum ether as eluent the fluoro ether **8**[7] was isolated as an oil in 75% yield: NMR δ 7.10 (10 H, m), 5.47 (1 H, dd, J_1 = 47 Hz, J_2 = 6.8 Hz), 4.46 (1 H, dd, J_1 = 14 Hz, J_2 = 6.8 Hz), 3.31 (3 H, s); ^{19}F NMR −180.74 ppm (dd, J_1 = 47 Hz, J_2 = 14 Hz).

Fluorination of 9 was carried out on 10 mmol according to method A using 20 mmol of AcOF. No reaction took place at −78 °C, but the starting material was fully consumed when the reaction mixture was allowed to warm up to 0 °C. After flash chromatography using 10% EtOAc in petroleum ether as eluent the fluoro ether **10** was isolated as an oil in 80% yield: IR 1685 cm^{-1}; NMR δ 6.5–7.20 (10 H, m), 5.40 (1 H, dd, J_1 = 50 Hz, J_2 = 3.5 Hz), 4.72 (1 H, dd, J_1 = 24 Hz, J_2 = 3.5 Hz), 3.23 (3 H, s); ^{19}F NMR −198.73 ppm (dd, J_1 = 50 Hz, J_2 = 24 Hz). Anal. Calcd for $C_{16}H_{25}FO_2$: C, 74.42; H, 5.81. Found: C, 74.70; H, 5.92.

Fluorination of 11 was carried out on 10 mmol according to method A using 30 mmol of AcOF. No reaction took place at −78 °C, but the starting material was fully consumed when the reaction mixture was allowed to warm up to 0 °C. In the crude reaction mixture two main compounds could be identified. The major component (**12**) has a doublet in the ^1H NMR spectroscopy at δ 4.65 (2 H, J = 48 Hz) and two singlets at δ 3.4 and 2.0 (3 H each). The minor derivative showed a triplet at δ 6.2 (1 H, J = 55 Hz) and two singlets at δ 3.47 and 2.1 (3 H each). After chromatography using 1% EtOAc in petroleum ether as eluent the less polar major compound was changed into the known **13**[11] in 44% overall yield: IR 1730 cm^{-1}; NMR δ 4.78 (2 H, d, J = 48 Hz), 2.52 (2 H, td, J_1 = 7 Hz, J_2 = 2.0 Hz), 1.6–1.07 (8 H, m) 0.88 (3 H, t, J = 7 Hz); ^{19}F NMR −228.27 ppm (t, J = 48 Hz); MS, m/e 146 (M^+), 113 [$(M - CH_2F)^+$], 85 [$(M - COCH_2F)^+$], 61 [$(COCH_2F)^+$]. The more polar derivative, which was unchanged by chromatography, was identified as the difluoro compound **14** isolated in 28% yield: IR 1750 cm^{-1}; NMR δ 6.20 (1 H, t, J = 55 Hz), 3.47 (3 H, s), 2.1 (3 H, s), 1.97 (2 H, t, J = 8 Hz), 1.6–1.0 (8 H, m) 0.88 (3 H, t, J = 7 Hz); ^{19}F NMR −131.85 (1 F, d, J = 55 Hz), −131.62 ppm (1 F, d, J = 55 Hz); MS, m/e 238 (M^+), 179 [$(M - OAc)^+$], 153 [$(C(OMe)(OAC)CHF_2)^+$]. Anal. Calcd for $C_{11}H_{20}F_2O_3$: C, 55.46; H, 8.40. Found: C, 55.73; H, 8.52.

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(15) Rozen, S.; Lerman, O. *J. Org. Chem.* **1980**, *45*, 672. See also ref 12.

Stereoelectronic Control in the Photolytic Cleavage of α-Chloro Ketones[1]

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The UV spectral perturbations created by a chlorine which is axial and α to a ketone have been known for some time[2] and have been attributed, in part, to a mixing of carbonyl π^* and C–Cl σ^* MO's to generate a new, lower-energy LUMO which is ($\pi^* + \sigma^*$).[3] Likewise, the facile

(1) Organic Photochemistry. 70. Part 69: Deibel, R. M.; Morrison, H.; Baird, W. M. *Photochem. Photobiol.* **1987**, *45*, 421.
(2) Cookson, R. C. *J. Chem. Soc.* **1954**, 282.

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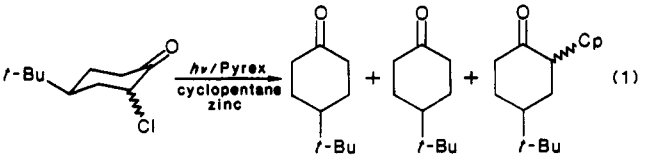
photolytic cleavage of a C–Cl bond α to a ketone has been observed in a number of cases,[4] and the involvement of σ^* character in the ground-state LUMO (and thus in the "n,π^*" excited state) has been invoked to rationalize such reactivity.[5] Though a preference for photolytic cleavage of an axial halogen could logically be inferred from the above,[5,6] such a stereoelectronic effect on the photochemistry has never been unambiguously demonstrated. Our interest in (π^* + σ^*) MO mixing as a mechanism for photoactivation of distal functionalities[7] led us to test for enhanced axial reactivity by studying α-halo cleavage in *cis*- and *trans*-4-*tert*-butyl-2-chlorocyclohexanone (**1e** and **1a**, respectively).

The two chloro ketones were prepared by the chlorination of 4-*tert*-butylcyclohexanone in 97% formic acid, purified by column chromatography, and either distilled (**1a**) or recrystallized (**1e**). NMR spectral data were identical with those of independently prepared samples.[8,9] The UV spectra in hexane [**1e**, λ_{max} 288 nm (ϵ 17); **1a**, λ_{max} 306 nm (ϵ 42)] match those in the literature[10] [**1e**, λ_{max} 286 nm (ϵ 17); **1a**, λ_{max} 306 nm (ϵ 49)] and illustrate the characteristic bathochromic and hyperchromic effects of an axial halogen.[2] Photolysis of each isomer was carried out in cyclopentane, through a Pyrex filter, using finely cut mossy zinc as an acid scavenger.[4a] The observed reactions are shown in eq 1 with each of the products identified by NMR and/or mass spectral analysis.[13] Analogous products were observed upon photolysis of α-chlorocyclohexanone in cyclohexane[4a,11] and can be attributed to C–Cl homolysis as the primary photochemical event.[14]



1e (ϕ_{dis} 0.18)	61%	7%	32%
1a (ϕ_{dis} 0.69)	67%	9%	24%

Quantum efficiencies for loss of **1e** and **1a**, measured by using the Norrish type 2 photochemistry of 2-hexanone for actinometry,[15] are also presented in eq 1. *The axial α-chloro isomer is observed to be almost 4-fold more photoreactive than the equatorial substrate, consistent with the proposed interrelationship between C–X σ^* mixing in the LUMO and photolytic C–X cleavage.*[16]

Experimental Section

^{1}H NMR were obtained with a Nicolet NT-470 (470 MHZ) spectrometer. Mass spectra were obtained with a Finnigan automated gas chromatography EI/CI mass spectrometer. Gas chromatography utilized a Varian Model 90P instrument for preparative work and Varian Model 1200 or 1400 FID chromatographs with a Hewlett-Packard 3380 or 3380-A digital integrator for quantitative studies. HPLC was done with a Waters Associates M-6000 pump equipped with an ISCO model 1840 variable wavelength uv detector and an H-P integrator. The quantum efficiency experiments were done with a rotating turntable surrounding a Canrad-Hanovia Model 679A, 450-W mercury source.

Photolysis of *cis*- and *trans*-4-*tert*-Butyl-2-chlorocyclohexanone (1e and 1a). In a typical procedure, 39 mg (0.21 mmol) of **1e** or **1a** was dissolved in 3 mL of cyclopentane (Burdick and Jackson Spectroquality) and transferred to a quartz photolysis tube. Finely cut mossy zinc (Aldrich) (1.0–1.5 g) was added to the tube, the solution was sparged with argon for 20 min, and the mixture was photolyzed in a water bath (25 °C) with an Hanovia 450-W mercury arc through a Pyrex filter for 15 h. Analysis for the disappearance of starting material was performed by HPLC using a 25 cm × 4.6 mm, 5 μm silica column (Alltech) with benzene as eluent. The variable wavelength UV detector was set at 300 nm, with retention times of 4.45 and 8.46 min for **1a** and **1e**, respectively (flow 1 mL/min). The products were analyzed by GC with an 8 ft × $^1/_8$ in. 5% Carbowax 20M on 60/80 mesh Chromosorb W (AW-DMCS) column at 170 °C (N_2 30 cm^3/min, H_2 30 cm^3/min, air 300 cm^3/min). Three products were detected. **4-*tert*-Butylcyclohexanone** (t_r 7.49 min) was purified by GC on a 20 ft × $^1/_4$ in. 10% FFAP on 60/80 mesh Chromosorb W (AW-DMCS) column at 170 °C and identified by comparison of its ^{1}H NMR ($CDCl_3$ 470 MHz) with a commercially available sample. **4-*tert*-Butyl-2-cyclohexenone** (t_r 10.64 min) was identified by GC/MS analysis on a 10% Carbowax 20M column (150 °C): mass spectra, (CI) m/e 153 (M^+ + H), (EI, 70 eV) 96, 57 (base peak). This product was isolated by GC admixed with **1a**; the ^{1}H NMR spectrum showed the two vinylic hydrogens at δ 6.05 and 7.05, each appearing as doublets. **4-*tert*-Butyl-2-cyclopentylcyclohexanone** (t_r 36.59 and 38.42 min). These cis and trans isomers were identified by GC/MS analysis as described above. The mass spectra associated with the two peaks were quite similar and do not permit the assignment of stereochemistry: mass spectra, (CI) 223 (M^+ + H), (EI, 70 eV) 153 (base peak, M – C_5H_9).

Quantum Efficiencies for Disappearance of 1a and 1e. These experiments were performed in duplicate with cyclopentane solutions (3 mL) of **1a** (3.21×10^{-2} M) and **1e** (5.80×10^{-2} M) together with 3 mL of solutions of 2-hexanone (1.0 M) in hexane (containing 4.3 mg of decane as an internal standard). The **1a** and **1e** solutions also contained finely cut mossy zinc. The **1a** and **1e** solutions were degassed with argon and photolyzed for 15 h as described above. Loss of **1a** and **1e** was determined by HPLC (see above). The degassed 2-hexanone solutions were photolyzed for 19 h and analyzed for acetone formation by GC on a 15 ft × $^1/_8$ in 20% Carbowax 20M on 60/80 mesh Chromosorb W (AW-DMCS) column at 110 °C (t_r 6.27 min (acetone), 11.66 min (decane)). The response factor equation was $A_A/A_D = 0.338W_A/W_D + 0.022$. The quantum efficiency for formation of acetone was taken as 0.22.[14] The relative amounts of light absorbed by **1a**, **1e**, and the 2-hexanone were calculated by using the measured filter transmittance, the lamp (mercury line) output at 280, 290, 296, 302, 313, and 334 nm (from Canrad-Hanovia), and the absorption characteristics of each ketone at these wavelengths (the typical intensity of light absorbed by 2-hexanone was 5.20×10^{14} photons/s). Measured quantum efficiencies were as follows: **1a**, 0.63, 0.75; **1e**, 0.18, 0.20.

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(3) Allinger, N. L.; Tai, J. C.; Miller, M. A. *J. Am. Chem. Soc.* **1966**, *88*, 4495. Levin, C. C.; Hoffmann, R.; Hehre, W. J.; Hudec, J. *J. Chem. Soc., Perkin Trans. 2* **1973**, 210.

(4) Recent examples: (a) Purohit, P. C.; Sonawane, H. R. *Tetrahedron* **1981**, *37*, 873. (b) Bergmark, W. R.; Barnes, C.; Clark, J.; Paparian, S.; Marynowski, S. *J. Org. Chem.* **1985**, *50*, 5612.

(5) Jones, G.; McDonnell, L. P. *J. Am. Chem. Soc.* **1976**, *98*, 6203. Zimmerman, H. E. *Acc. Chem. Res.* **1982**, *10*, 312.

(6) Calculations on α-chlorocyclohexanone, by using Gaussian 76 with an STO-3G basis set, indicate significant σ^* mixing in the LUMO's of *both* the axial *and* the equatorial isomers but appreciably more so for the axial case.[7a]

(7) (a) Morrison, H.; Singh, T. V.; de Cardenas, L.; Severance, D.; Jordan, K.; Schaefer, W. *J. Am. Chem. Soc.* **1986**, *108*, 3862. (b) Morrison, H. *Rev. Chem. Intermed.*, in press.

(8) Thorpe, J. W.; Warkentin, J. *Can. J. Chem.* **1973**, *51*, 927. Denmark, S. E.; Dappen, M. S. *J. Org. Chem.* **1984**, *49*, 798.

(9) We are grateful to Professor Denmark for providing authentic spectra.

(10) Allinger, N. L.; Allinger, J.; Freiberg, L. A.; Czaja, R. F.; LeBel, N. A. *J. Am. Chem. Soc.* **1960**, *82*, 5876.

(11) These workers observe a ca. 2:1 ratio of solvent (cyclohexane) incorporated product and cyclohexanone, the inverse of what we see in eq 1 (in cyclopentane); the difference may be attributed to cyclopentane acting as a better hydrogen atom donor.[12]

(12) Wilt, J. W. *J. Org. Chem.* **1960**, *25*, 891 and references therein.

(13) There is no evidence for **1a** $\rightleftharpoons$ **1e** isomerization.

(14) The 4-*tert*-butylcyclohexenone could also be derived from a carbocation precursor,[4a] for which there is precedent in α-chloro ketone photochemistry (cf. ref 4 and references therein).

(15) Wagner, P. J. *Tetrahedron Lett.* **1968**, 5795.

(16) It is assumed that radiationless decay rates competing with photodissociation are not significantly enhanced in **1e** relative to **1a**. There is no evidence for appreciable internal return for either isomer.[13]

search. The 470-MHz NMR data were obtained through the Purdue University Biological Magnetic Resonance Laboratory (Grant NIH-RR01077) and the GC-MS data were obtained on an instrument provided by NSF Grant CHE-8010832.

Monoacylation of Symmetrical Diamines

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Diamines are often used as spacer elements between two dissimilar carboxylic acid components for the synthesis of biologically active agents, such as interconnecting two receptor pharmacophores to form unsymmetrical "bivalent ligands",[1] interconnecting a pharmacophore with an alkylating or photolabile group to form affinity labels,[2] or in the synthesis of unsymmetrically substituted polyamines.[3-6] These syntheses require a strategy which depends upon the selective monoacylation of one end of the diamine. A 1:1 stoichiometry of diamine and acylating agent corresponds to the statistical prediction of 50% yield of the desired monoamide (with 25% yield of both diamide and unreacted diamine), which is synthetically acceptable only if these three materials are easily separated and the acylating component is expendable. On the other hand, the utilization of excess diamine should greatly increase the yield of monoamide based on acylating agent. In cases where the diamine is volatile (e.g., ethylenediamine) or otherwise easily separable, high isolated yields of monoacylated diamine should be readily obtained through this approach. It is thus surprising to note the many examples in the literature wherein it is reported that the employment of excess diamine (sometimes as the solvent) yields inordinately large amounts of diacyl byproduct.[6-10] Such findings prompted these and other investigators to utilize alternative strategies for obtaining the desired monoacyl product, often involving a time-consuming protection–acylation–deprotection sequence[2,4,9-12] or de novo synthesis.[13]

Table I. Yield of Diacyl Product from the Reaction of 1,2-Ethanediamine (EDA) or 1,4-Butanediamine (BDA) (10 mmol) with Various Acylating Agents (2 mmol)[a]

		diacyl product formed,[b] mmol	
diamine	RCOX	"standard"[c]	"high-dilution"[d]
EDA	PhCOCl	0.99	0.22
EDA	$(PhCO)_2O$	0.24	0.14
EDA	$PhCH_2COCl$	0.89	0.56
EDA	$(PhCH_2CO)_2O$	0.29	0.07
EDA	$PhCH_2COOSu$	0.07	0.06
BDA	PhCOCl	0.79	0.35
BDA	$(PhCO)_2O$	0.27	0.09

[a] Data represent the average of two to four experiments. [b] Statistically predicted yield is 0.1 mmol; maximum possible yield is 1.0 mmol. [c] RCOX in 5 mL of CH_2Cl added to diamine in 15 mL of CH_2Cl_2 at -78 °C. [d] RCOX in 100 mL of CH_2Cl_2 added to diamine in 300 mL of CH_2Cl_2 at -78 °C.

Although several possible explanations for the formation of abnormally large amounts of diacyl material are certain to have been considered (e.g., intramolecular catalysis by the first-formed amide group or some other effect that makes the initial monoamide more reactive than unacylated diamine), the invariance of the observed "diacyl effect" with structure of the diamine[6-10] suggests that the only rational explanation is that of a mixing problem. That the limitations of mixing could contribute to the production of difunctionalized diamine in much higher than statistical yield was pointed out many years ago for the reaction of diamines with isocyanates and isothiocyanates,[7] wherein it was shown that the more reactive (former) reagent gave more diacyl product than did the less reactive (latter) reagent. Unfortunately, most organic chemists are unaware of this study and probably believe that a slow dropwise addition of a reasonably dilute solution of an acid chloride to a well-stirred solution of diamine at low temperature (e.g., -78 °C) results in a more-or-less complete dispersion of reactants (at a molecular level) prior to reaction. Once one recognizes that this might not be the case, it is easy to modify reaction conditions to reduce the formation of diacyl material to the statistical limit.

We carried out a simple study comparing the product distribution of a monoacylation experiment as a function of (1) the reactivity of the acylating agent and (2) the concentration of reactants, independently, for two representative amines, 1,2-ethanediamine (EDA) and 1,4-butanediamine (BDA). *Our findings confirm that a typical acylation protocol using an acid chloride results in predominantly diacyl product even though the diamine is present in fivefold excess. On the other hand, the combination of increasing reactant dilution and decreasing reactivity of the acylating agent results in a statistical product distribution.*

Results

Table I lists the results of adding the aryl acylating agents benzoyl chloride or benzoic anhydride to a fivefold excess of either 1,2-ethanediamine or 1,4-butanediamine, under either "standard" or "high-dilution" conditions (see Experimental Section), in CH_2Cl_2 with rapid stirring at -78 °C. In the case of EDA, results were also obtained by using three aliphatic acylating agents, including a *N*-hydroxysuccinimide (HOSu) "active ester" commonly used in peptide chemistry. The 1:5 stoichiometry corresponds to

(1) Triggle, D. J. *Trends Pharmacol. Sci.* **1983**, *4*, 107.
(2) Zioudrou, C.; Varoucha, D.; Loukas, S.; Nicolaou, N.; Streaty, R. A.; Klee, W. A. *J. Biol. Chem.* **1983**, *258*, 10934.
(3) Hansen, J. B.; Nielsen, M. C.; Ehrbar, U.; Buchardt, O. *Synthesis* **1982**, 404.
(4) Jackson, E. L. *J. Org. Chem.* **1956**, *21*, 1374.
(5) Tabor, H.; Tabor, C. W.; De Meis, L. *Methods Enzymol.* **1971**, *17B*, 829.
(6) Bergeron, R. J.; Garlich, J. R.; Stolowich, N. J. *J. Org. Chem.* **1984**, *49*, 2997.
(7) Stoutland, O.; Helgen, L.; Agre, C. L. *J. Org. Chem.* **1959**, *24*, 818.
(8) Moore, T. S.; Boyle, M.; Thorn, V. M. *J. Chem. Soc.* **1929**, 39.
(9) Lawson, W. B.; Leafer, M. D., Jr.; Tewes, A.; Rao, G. J. S. *Hoppe-Seyler's Z. Physiol. Chem.* **1968**, *349*, 251.
(10) Stahl, G. L.; Walter, R.; Smith, C. W. *J. Org. Chem.* **1978**, *43*, 2285.
(11) (a) Schwartz, E.; Shanzer, A. *Tetrahedron Lett.* **1982**, *23*, 979. (b) Barker, P. L.; Gendler, P. L.; Rapoport, H. *J. Org. Chem.* **1981**, *46*, 2455.
(12) A polymer-based protecting group strategy has been employed as a method of achieving effective high-dilution (by controlling the average spacing between groups) and, consequently, selective monofunctionalization: Dixit, D. M.; Leznoff, C. C. *J. Chem. Soc., Chem. Commun.* **1977**, 798.
(13) (a) Kunesch, G. *Tetrahedron Lett.* **1983**, *24*, 5211. (b) Kagiya, T.; Izu, M.; Matsuda, T.; Matsuda, M.; Fukui, K. *J. Polym. Sci., Polym. Chem. Ed.* **1968**, *6*, 2059. (c) Nakajima, K.; Shinuchi, T.; Tauchi, M. *Nippon Kagaku Zasshi* **1967**, *88*, 976.

0022-3263/87/1952-2592$01.50/0