mixture was stirred for 2 h at 5 °C in an ice bath. Room temperature stirring for 1 h was followed by overnight standing. The solution was diluted with 150 mL of ice water and extracted with four 50-mL portions of ether. This ether solution was dried (Na$_2$SO$_4$), concentrated, and fractionally distilled, giving a 30% yield[13] of 1, in four fractions, bp 92–98 °C (0.2 torr), as clear liquid and white crystals, 80–97% pure by VPC. The instantaneous positive FeCl$_3$ test (purple) showed the highly enolic character,[14] estimated at ~95% via NMR integrals.

Methyl Enol Ethers of α-Acetyl-δ-valerolactone (A and B).[15] Diazomethane[16] was prepared in ethereal solution, 76% yield, from the reaction of *N,N'*-dinitroso-*N,N'*-dimethylterephthalamide in mineral oil with sodium hydroxide in Carbitol and ether. To the ether solution of diazomethane, at room temperature, was added 6.02 g of 1 dissolved in methanol. The solution was protected from light and moisture for the 5 days of reaction time. Excess CH$_2$N$_2$ was destroyed with 2 N HOAc. The colorless solution, washed with cold 2 N NaOH followed by H$_2$O, was dried over anhydrous Na$_2$SO$_4$. Flash distillation, followed by repeated fractional vacuum distillations, yielded the A and B isomers in a 1:3 ratio, 56% total yield. A: bp 80–82 °C (0.06 torr); λ$_{max}$ (MeOH) 260 nm (11 800); IR 2950, 1692, 1595, 1285, 1097 cm^{-1}; NMR δ 1.76 (m, 2 H), 2.39 (m, 5 H), 3.76 (s, 3 H), 4.07 (t, 2 H); MS 156 (M$^+$), 141 (M – CH$_3$), 43 (base, CH$_3$CO). B: bp

69 °C (0.09 torr); λ$_{max}$ (MeOH) 272 nm (15 900); IR 2958, 1618 (sh), 1576, 1377, 1160 cm^{-1}; NMR δ 1.78 (m, 2 H), 2.14 (s, 3 H), 2.18 (t, 2 H), 3.77 (s, 3 H), 4.18 (t, 2 H); MS 156 (M$^+$), 141 (M – CH$_3$), 113, 109, 43 (base, CH$_3$CO).

Dipole Moment Measurements.[9b-11] Repeated vacuum distillations provided pure samples of the isomeric enol ethers, A and B. For the quantitatively prepared 100-mL solutions, in benzene, approximately 4, 3, 2, and 1 mol % carefully measured solute weights and densities were used in the mole fraction determinations. Capacitance of solution measurements, *C*, were compared with that of air, C_0, for the dielectric constant values, $\epsilon = C/C_0$. Refractive indices of the solvent, n_1, and the solutions were measured. With these data, calculations of the molar orientation polarization at infinite dilution, $P_{2\mu}°$, and the dipole moments, μ, were made using the equations $P_{2\mu}° = Ca - 3Bc/(n_1^2 + 2)^2$[17] and $μ = 0.0128 (P_{2\mu}°T)^{1/2} \times 10^{-18}$ D, where *a* = slope of plot of dielectric constants vs. mole fraction of solute, *c* = slope of plot of squares of indices of refraction vs. mole fraction of solute, *B* = molecular weight of solvent/$\rho_{solvent}$, and *C* = 3 (molecular weight of solvent)/(dielectric constant + 2)^2 × $\rho_{solvent}$. The averages of the results for duplicate determinations of the dipole moments were as follows: (*Z*)-ether, B, $P_{2\mu}° = 443$ cm^3/m, μ = 4.65 ± 0.02 D; (*E*)-ether, A, $P_{2\mu}° = 404$ cm^3/m, μ = 4.44 ± 0.01 D.

(13) The separation of the self-condensation product, ethyl acetoacetate, as well as the removal of unreacted δ-valerolactone required repeated procedures and purifications before the ether preparations were carried out.

(14) This intermediate had not previously been prepared. White platelets: mp 42–43 °C from petroleum ether (bp 50–60 °C); IR broad OH band characteristic of chelated enol, 1735 (ester C=O), 1717 (ketone C=O), 1636 (str, enol C=O), 1610 cm^{-1} (str, enol C=C); NMR (CCl$_4$) δ 13.73 (enolic H).

(15) An adaptation of the method of: Arndt, F.; Loewe, L.; Severge, T.; Türegün, I. *Chem. Ber.* **1938**, *71*, 1640.

(16) Moore, J. A.; Reed, D. E. *Org. Synth.* **1961**, *41*, 16.

(17) This involved the use of the Smith[11] assumption since the refractive index of the solute could not be measured directly and the dielectric constant of the solvent, benzene, was, as required, approximately equal to the square of its refractive index.

Communications

Preparation of Benzocyclobutenols from *o*-Halostyrene Oxides

Summary: Reaction of several *o*-bromo- and *o*-iodostyrene oxides, dissolved in THF at −78 °C containing a suspension of MgBr$_2$, with *n*-BuLi gave benzocyclobutenols in 50–83% yield.

Sir: Our work on the Grignard-reagent-induced cyclization of γ-epoxy sulfones[1,2] and γ-epoxy nitriles[1] (eq 1), coupled with the report by Bradsher and Reames[3] that metalation of the *o*-brominated epoxides 1 with *n*-butyllithium gave the intermediate 2 without interference from the epoxide function, suggested that ortho-halogenated styrene oxides 3 might possibly serve as precursors to benzocyclobutenols 4.[4] As is reported in this communication, this expectation has been realized.

Thus reaction of **3b**, dissolved in THF at −78 °C containing 2 equiv of suspended MgBr$_2$, with *n*-BuLi for 30 min, followed by warming to room temperature, afforded

benzocyclobutenol (**4**) [^{1}H NMR[5] δ 2.28 (OH), 3.30 (dd, *J* = 14, 2 Hz, 1 H), 3.59 (dd, *J* = 14, 4.5 Hz, 1 H), 5.28 (dd, *J* = 4.5, 2 Hz, 1 H), 7.1–7.4 (m, 4 H); mp 56–58 °C (lit.[6] 58 °C)] in yields up to 83%.[7] The formation of **4** was equally successful from *o*-iodostyrene oxide (**3c**).

Benzocyclobutenol was also obtained from **3b**, albeit in only 40% yield, when the metal–halogen exchange was carried out with *n*-BuLi at −78 °C for 5 min followed by addition of 2 equiv of MgBr$_2$ (2.5 M in ether). Longer time intervals between the *n*-BuLi and MgBr$_2$ additions decreased the yield of **4** even further and gave crude products whose NMR spectrum showed considerable butyl group absorption. No **4** was obtained in the absence of MgBr$_2$.

In contrast to the results obtained with the *o*-bromo and *o*-iodo derivatives, *o*-chlorostyrene oxide (**3a**) gave no **4** under the above conditions. When **3a** was metalated at −95 °C in THF for 15 min and the reaction mixture was allowed to warm to room temperature prior to addition of a saturated NH$_4$Cl solution, an *E/Z* mixture of the unusual stilbene derivative **5** was formed in about 50% yield. The two isomers were separated by column chromatography

(1) B. Corbel and T. Durst, *J. Org. Chem.*, **41**, 3648 (1976).

(2) B. Corbel, J. M. Decesare, and T. Durst, *Can. J. Chem.*, **56**, 505 (1978).

(3) C. K. Bradsher and D. C. Reames, *J. Org. Chem.*, **43**, 3800 (1978).

(4) Benzocyclobutene derivatives have been shown to be valuable intermediates in the synthesis of steroids and alkaloids: W. Oppolzer, *Synthesis*, 793 (1978).

(5) These values differ from those reported by Arnold et al.: B. J. Arnold, S. M. Mellows, P. G. Sammes, and T. W. Wallace, *J. Chem. Soc., Perkin Trans. 1*, 401 (1974). In particular, the vicinal coupling constants were erroneously reported and should be reversed. The hydrogen cis to the OH group occurs at lower fied than that which is trans.

(6) M. P. Cava and K. Muth, *J. Am. Chem. Soc.*, **82**, 652 (1960).

(7) In a number of experiments the yield of **4** ranged from 60 to 83%.

EWG = PhSO$_2$, CN

(1)

(2)

3a, X = Cl
b, X = Br
c, X = I

(3)
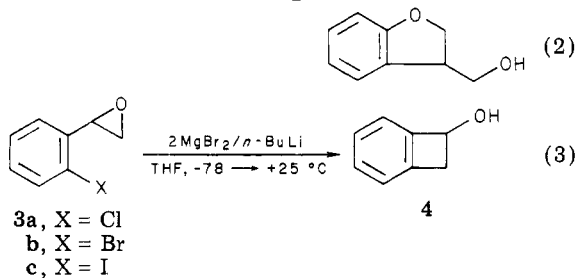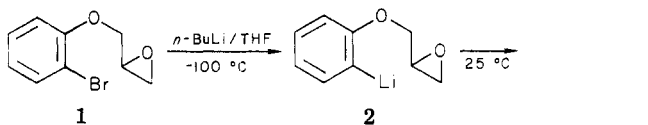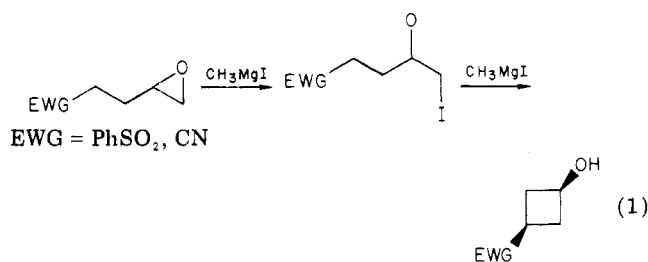
on silica gel. The gross structure of one of the isomers, mp 121–121.5 °C, was assigned on the basis of its elemental analysis, NMR spectra,[8] and conversion to a crystalline diacetate (mp 85–86 °C) and a yellow dialdehyde (mp 115–117 °C) upon treatment with MnO$_2$ in refluxing benzene. In the case of 3a it appears that abstraction of a benzylic hydrogen is favored over chlorine–lithium exchange.[9] The metalation of some styrene oxides has been reported by Eisch and Galle.[10]
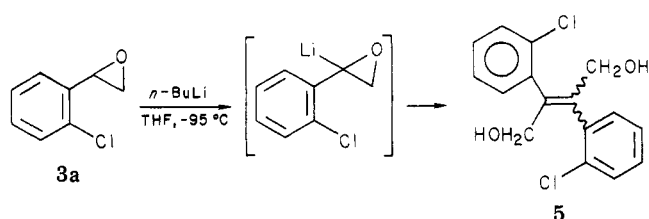

Other ortho-halogenated sytrene oxides which have been converted to benzocyclobutenols are the 2-bromo-5-methoxy (7), 2-iodo-5-methoxy (8), and β-methyl-2-bromo (9) derivatives.[12,13]

The product obtained from the epoxides 7 and 8 was the benzocyclobutanol 10. This compound was obtained as a colorless oil in 70%[14] and 72% yield from 7 and 8, respectively, after purification by column chromatography. Its structure was proved by elemental analysis and its proton NMR spectrum which showed the expected ABX pattern due to three hydrogens of the cyclobutene ring.[15] More importantly, treatment of 10 with aqueous NaOH

Scheme I
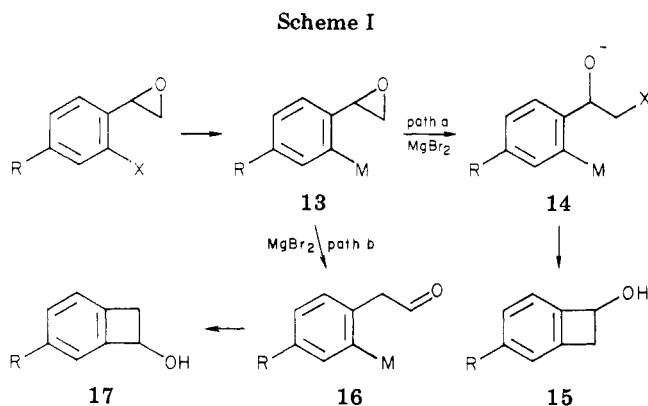
gave 2-methyl-4-methoxybenzaldehyde[16] which was further oxidized by air to 2-methyl-4-methoxybenzoic acid, mp 175–179 °C (lit.[17] 177–178 °C).

In contrast, the β-methylstyrene oxide 9 reacted under our conditions to give an inseparable 2:1 mixture of the benzocyclobutanols 11 and 12 in about 50% overall yield. Key aspects of the ^{1}H NMR spectrum of the mixture were a singlet and a doublet CH$_3$ group at δ 1.62 and 1.34 due to 12 and 11, respectively, a multiplet at δ 3.2–3.4 (2 H) due to both compounds, and a closely spaced doublet at δ 4.68, due to the CHOH having a small trans coupling. The ^{13}C spectrum of the mixture showed six nonaromatic carbons: 16.6 (q), 50.4 (d), and 77.7 (d), assigned to 11, and 25.7 (q), 48.0 (t), and 78.7 (s), in agreement with structure 12.

7, X = Br
8, X = I

10

9   11   12
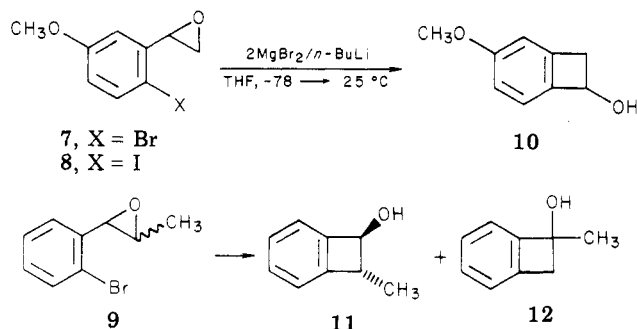
The formation of 10 from 7 and 8 is best rationalized if one assumes that the intermediate lithiated epoxide 13[18] rearranged in the presence of MgBr$_2$ to the ortho-metalated aldehyde 16 (path b in Scheme I) which then undergoes cyclization. Such a pathway would also account for the formation of the tertiary alcohol 12 from 9 The concurrent formation of the secondary alcohol 11 may be envisaged as proceeding via the opening of the epoxide to a bromo alkoxide[1] followed by cyclization (path a, Scheme I). Further studies designed to verify the above mecha-

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(8) ^{1}H NMR δ 3.9–4.3 (m, 4 H), 4.7 (2 OH), 7.2–7.5 (m, 8 H).

(9) A plausible mechanism[11] for the formation of 5 involves reaction of the lithio epoxide 6 with the carbene ARCCH$_2$OLi resulting from the ring opening of 6.[10]

(10) J. J. Eisch and J. E. Galle, *J. Organomet. Chem.*, 121, C10 (1976).

(11) B. D. Gowland, M.Sc. Thesis, University of Ottawa, 1978.

(12) The preparation of these compounds followed standard literature procedures. The precursor o-halobenzaldehydes were converted to the epoxides by reaction with trimethylsulfonium chloride under phase-transfer catalysis.

(13) All new structures were adequately characterized by proton and carbon-13 NMR spectroscopy, IR spectroscopy, and elemental analysis.

(14) Based on 50% recovered starting material.

(15) ^{1}H NMR δ 2.5 (OH), 2.94 (dd, J = 14, 15 Hz, 1 H), 3.50 (dd, J = 14, 4.5 Hz, 1 H), 3.76 (s, 3 H), 5.18 (dd, J = 4.5, 1.5 Hz), 6.6–7.2 (m, 3 H); ^{13}C NMR 41.7, 55.4, 70.0, 108.9, 114.0, 123.6, 139.8, 143.4, 161.1 ppm. The proton NMR spectrum differs significantly from that reported for the other possible isomer, 17 (R = OCH$_3$): T. Kametani, Y. Katoh, and K. Fukumoto, *J. Chem. Soc., Perkin Trans. 1*, 712 (1974). The NMR spectra of the crude reaction products from 7 and 8 indicated no significant contamination by this other isomer.

(16) ^{1}H NMR δ 2.63 (s, 3 H), 3.86 (s, 3 H), 6.7–6.9 (m, 2 H), 7.69 (d, J = 8 Hz, 1 H), 10.08 (s, 1 H).

(17) P. Hill, W. F. Short, H. Stromberg, and A. E. Wiles, *J. Chem. Soc.*, 510 (1937).

(18) The metalation precedes reaction of the epoxide with MgBr$_2$ since quenching of the reaction mixture from 3b prior to warming above –78 °C yields styrene oxide (>90%). The intermediate 13 can also be trapped with acetone.
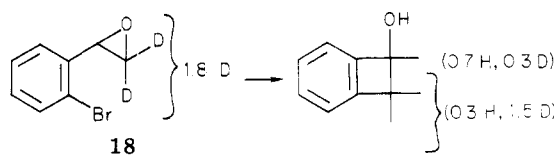
nistic proposals and to delineate more clearly the effect of substituents, both on the aromatic ring and on the epoxide ring, on the course of the reaction are in progress.

In agreement with the above two-path process is the observation that β,β-dideuterio-*o*-styrene oxide **18**, prepared from *o*-bromobenzaldehyde and trimethylsulfonium chloride in $D_2O/NaOD/PhCH_2^+N(Et)_3Cl^-$, gave benzocyclobutenol in which the deuterium labels were found to the extent of 0.3 atoms of D on the carbon bearing the hydroxyl group and 1.5 atoms of D at the methylene carbon. The results suggest that **3b** is converted to **4** by a combination of path a (70%) and path b (30%).

A typical procedure follows: 492 mg (2.0 mmol) of *o*-iodosytrene oxide was dissolved in 30 mL of dry THF at −78 °C under N_2. To this was added 1.6 mL of $MgBr_2$ (2.5 M in ether) which caused a white precipitate, followed by 1.4 mL of *n*-BuLi (1.6 M in hexane). The reaction mixture was stirred for 15–20 min at −78 °C, allowed to warm to room temperature, and quenched with saturated NH_4Cl solution. Typical workup followed by chromatography of the crude product on silica gel (1:2 ethyl acetate–hexane eluent) gave 200 mg (83%) of benzocyclobutenol, mp 56–58 °C.

Finally, as expected from our previous results, the epoxides **1**[3] can be converted in good yield into the six-membered-ring derivatives **19** if the metalation is carried out with *n*-BuLi in THF at −78 °C in the presence of $MgBr_2$ or at −100 °C with *n*-BuLi[3] followed by addition of $MgBr_2$ at −78 °C and subsequent warming to room temperature. These results again point out the value of the $RLi/MgBr_2$ combination in the various intramolecular epoxide ring-opening reactions.
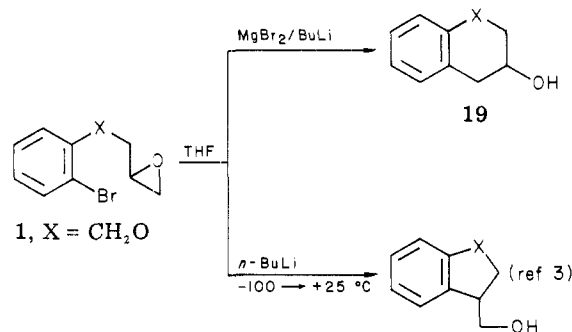
Registry No. 1 (X = CH₂), 71813-52-0; 1 (X = O), 22421-56-3; **3a**, 62717-50-4; **3b**, 71636-51-6; **3c**, 72525-47-4; **4**, 35447-99-5; **5** (*E* isomer), 72525-48-5; **5** (*Z* isomer), 72525-49-6; **7**, 72525-50-9; **8**, 72525-51-0; **9**, 72525-52-1; **10**, 72525-53-2; **11**, 72525-54-3; **12**, 19164-60-4; **18**, 72525-55-4; **19** (X = CH₂), 530-91-6; **19** (X = O), 21834-60-6; 2-methyl-4-methoxybenzaldehyde, 52289-54-0; 2-methyl-4-methoxybenzoic acid, 6245-57-4.

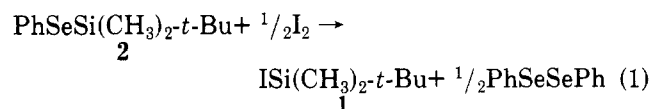**Kasturi L. Dhawan, Barbara D. Gowland**
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Electrophilic Conversion of Oxiranes to Allylic Alcohols with *tert*-Butyldimethylsilyl Iodide

Summary: *tert*-Butyldimethylsilyl iodide (**1**) is prepared from the reaction of iodine with (phenylseleno)-*tert*-butyldimethylsilane in acetonitrile. The reaction of oxiranes with **1** followed by treatment with 1,5-diazabicyclo-[4.3.0]non-5-ene gives acceptable yields of allylic alcohols isolated as their *tert*-butyldimethylsilyl ethers. Ring opening involves cleavage of the bond to the more highly substituted carbon.

Sir: Oxiranes have been isomerized to allylic alcohols by a variety of reagents including organoselenium compounds,[1] dialkylaluminum amides,[2] dialkylboron trifluoromethanesulfonates,[3] and various lithium dialkylamides.[4] Recently, a method was reported for rearranging oxiranes to allylic alcohols with trimethylsilyl trifluoromethanesulfonate.[5] This method is satisfactory for cyclic 2,2-di-, tri-, and tetrasubstituted oxiranes but fails with acyclic 2,3-dialkyl- and monoalkyloxiranes. In this communication, we report a more general procedure using *tert*-butyldimethylsilyl iodide (**1**, TBDSI) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN). The reaction conditions are mild, and the method is satisfactory for cyclic di-, tri-, and tetrasubstituted oxiranes. The allylic alcohols are obtained as the hydrolytically stable *tert*-butyldimethylsilyl ethers.[6] Regiochemical results parallel those reported for trimethylsilyl trifluoromethanesulfonate, but some significant differences are noted.

$$PhSeSi(CH_3)_2\text{-}t\text{-}Bu + \frac{1}{2}I_2 \rightarrow$$
$$\mathbf{2}$$
$$ISi(CH_3)_2\text{-}t\text{-}Bu + \frac{1}{2}PhSeSePh \quad (1)$$
$$\mathbf{1}$$

Treatment of (phenylseleno)-*tert*-butyldimethylsilane (**2**)[7] with 0.5 equiv of iodine in acetonitrile gave **1** and diphenyl diselenide as the only products (eq 1). Attempted isolation of TBDSI by vacuum sublimation gave a white solid that rapidly turned to a red oil containing iodine and bis(*tert*-butyldimethyl)disilane. Therefore, the reagent was generated and used in situ.

Reactions with oxiranes were run by generating **1** in an addition funnel under argon and adding this solution dropwise to a cooled (0 °C) solution of substrate in acetonitrile. Immediately after the addition, the reaction mixture was diluted with saturated sodium bicarbonate solution. The products were extracted with methylene chloride, and the extract was dried and concentrated. The residue was taken up in tetrahydrofuran (THF) and 1.5

(1) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 2697.
(2) Yasuda, A.; Tanaka, S.; Oshima, K.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1974**, *96*, 6513. Yamamoto, H.; Nozaki, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 169.
(3) Inoue, T.; Uchimara, T.; Mukaiyama, T. *Chem. Lett.* **1977**, 1214.
(4) For example and references cited therein: Whitesell, J. K.; White, P. D. *Synthesis* **1975**, 602. Sheng, M. N. *Ibid.* **1972**, 194. Kissel, C. L.; Rickborn, B. *J. Org. Chem.* **1972**, *37*, 2060. Rickborn, B.; Thummel, R. P. *Ibid.* **1969**, *34*, 3583. Cope, A. C.; Berchtold, G. A.; Peterson, P. E.; Sharman, S. H. *J. Am. Chem. Soc.* **1960**, *82*, 6370.
(5) Murata, S.; Suzuki, M.; Noyori, R. *J. Am. Chem. Soc.* **1979**, *101*, 2739.
(6) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190.
(7) Selenosilane 2 [bp 60–52 °C (0.2 torr)] was prepared from diphenyl diselenide, sodium, and *tert*-butyldimethylsilyl chloride in THF in a manner analogous to the procedure described in: Detty, M. R. *Tetrahedron Lett.* **1978**, 5087.
(8) Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *J. Org. Chem.* **1979**, *44*, 1247. Jung, M. E.; Blumenkopf, T. A. *Tetrahedron Lett.* **1978**, 3657. Ho, T.-L.; Olah, G. A. *Synthesis* **1977**, 417.