accomplished by reaction with AlH_3/THF at 0 °C for 30 min to afford (S)-2-(mesyloxy)-1-propanol (5) in high yield. This material proved to be extremely sensitive and decomposed vigorously upon attempted distillation[7]; however, it was smoothly converted to (+)-(R)-methyloxirane (2) upon slow addition to 66% aqueous KOH at 70 °C in a flask equipped with a distillation head. Redistillation of the wet distillate from KOH pellets afforded a 71% overall yield of 2 [bp 33-34 °C (730 mm); $[\alpha]^{22}_D$ +13.0° (neat)],[4,8] from ethyl (+)-(S)-lactate (3). The conditions for the cyclizations are critical since 5 appears to be extremely prone to polymerization under basic conditions. Attempts to form the epoxide under a variety of conditions (NaH/DMF, Na/ethylene glycol, KO-t-amyl/t-amyl alcohol, DBU/diglyme, Na_2CO_3/H_2O, K_2CO_3/EtOH, $LiN(SiMe_3)_2$) resulted in poor yields of epoxide.

Experimental Section

General Methods. Boiling points are uncorrected. Infrared spectra were obtained on films by using a Beckman Acculab 1 spectrophotometer. Nuclear magnetic resonance spectra were obtained in $CDCl_3/Me_4Si$ on a Varian Associates EM-360 spectrometer. Gas chromatograms were obtained on a Varian Aerograph Series 1700 instrument using 3 mm × 2.2 m glass columns packed with 3% OV-17 on 80/100 Chromosorb W-HP. Optical rotations were obtained on a Rudolph polarimeter in 1-dm cuvettes. Thin-layer chromatograms were run by using 250-μm Merck precoated silica gel layers.

Ethyl (-)-(S)-2-(Mesyloxy)propanoate (4). Redistilled ethyl (+)-(S)-lactate (3; 82.0 g, 0.695 mol) was combined with triethylamine (111.0 mL, 0.798 mol) in 1 L of toluene in a 2-L round-bottomed flask equipped with a magnetic stirrer. The mixture was cooled in an ice bath while methanesulfonyl chloride (56.6 mL, 0.73 mol) was added over a 15-min period. The light orange solution was kept an additional hour in the ice bath and then stored in a freezer (-15 °C) overnight. The mixture was then allowed to warm to room temperature, filtered (suction), and concentrated at reduced pressure to a light brown oil. Distillation through a 130-mm Vigreux column afforded 133 g (98%) of 4:[6] bp 75-76 °C (0.03 mm); $[\alpha]^{22}_D$ -52.9° (c 4.32, $CHCl_3$). This was shown by gas chromatography to be >99% pure (retention time, 2.0 min at 160 °C): NMR ($CDCl_3$) δ 5.15 (1 H, q, J = 7 Hz), 4.33 (2 H, q, J = 7.5 Hz), 3.15 (3 H, s), 1.62 (3 H, d, J = 7 Hz), 1.35 (3 H, t, J = 7.5 Hz).

(S)-2-(Mesyloxy)-1-propanol (5). The method of Brown[9] for the large-scale preparation of AlH_3 was modified. A 1-L three-necked flasked equipped with an N_2 inlet, a reflux condenser, and a large stirring bar was charged with 200 mL dry THF and 111.0 mL of a solution[10] of $LiAlH_4$ in THF (1.25 M, 0.139 mol). The flask was placed in an ice bath, and 100% H_2SO_4 (3.7 mL, 0.07 mol) was added cautiously. After 1 h, the mixture was cooled to -5 °C, and the ester 4 (23.5 g, 0.120 mol) in 50 mL THF was added during 10 min. After 30 min, the mixture was quenched with 20 mL of a 1:1 THF-H_2O solution followed by an additional 10-mL portion of H_2O and then stirred for 20 min before it was filtered (suction). The filter cake was washed with 100 mL of THF, 25 mL H_2O, and two additional 100-mL portions of THF. The filtrate was dried with anhydrous magnesium sulfate and concentrated at reduced pressure to afford 18.5 g of 5 as a yellow oil containing a small amount of suspended salts. This material could not be distilled without vigorous decomposition and was used directly in the next step without further handling. By thin-layer chromatography (25% petroleum ether-75% ether) the reaction was complete, and no ethyl ester remained: NMR ($CDCl_3$) δ 5.1-4.6 (1 H, m), 3.78 (2 H, d, J = 5 Hz), 3.15 δ (3 H, s), 2.92 (1 H, s), 1.42 (3 H, d, J = 7 Hz).

(+)-(R)-Methyloxirane (2). In a 250-mL round-bottomed flask equipped with a septum-sealed sidearm, a magnetic stirrer, and a distillation head were placed 100 g KOH and 50 mL of H_2O. The flask was heated to 70 °C, and then the mesylate 5 (18.5 g) was added dropwise with a syringe through the sidearm. The epoxide began to distill immediately. After the addition, a 25-mL portion of H_2O was added, and the temperature increased to 90 °C. After evolution of the epoxide ceased, the receiving flask was removed and the wet distillate redistilled from KOH pellets to afford 2: 5.0 g (72% from 4); bp 33-34 °C (730 mm); $[\alpha]^{22}_D$ +13.0° (neat)[8]; shown by gas chromatography to be >99% pure (retention time 0.5 min at 40 °C). This material was spectroscopically identical with a sample of racemic material.

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Registry No. 2, 15448-47-2; 3, 687-47-8; 4, 63696-99-1; 5, 77965-71-0.

(7) Havbrandt, O.; Osterman-Golkar, S.; Wachtmeister, C. A. *Acta Chem. Scand.* **1969**, *23*, 1072. These authors report vigorous decomposition of the racemic hydroxymesylates during attempted distillation. The compound appears to be stable below -15 °C for extended periods.

(8) Literature values reported for the rotation of (+)-(R)-methyloxirane are as follows: (a) $[\alpha]^{16}_D$ +12.53° (neat), Kumata, Y.; Furukawa, J.; Fueno, T. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3920. (b) $[\alpha]^{24}_D$ +13.9° (neat).[3a] (c) $[\alpha]^{20}_D$ +11.25° (neat).[3d] On the basis of our observed rotation for ethyl lactate, this preparation of (+)-(R)-methyloxirane was accomplished with no appreciable racemization.

(9) Yoon, N. M.; Brown, H. C. *J. Am. Chem. Soc.* **1968**, *90*, 2927.

(10) Suspended material from $LiAlH_4$ if not removed by filtration results in reduced yield of 5.

Lithiation of *N,N*-Dimethylmethallylamine

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The generation of allylic anions derived from allylic ethers,[1] carbamates,[2] thioethers,[3] and amines[4] and their use as homoenolate equivalents have received widespread attention in recent years. In all these cases deprotonation takes place at the α position, producing typical allylic anions in which the α/γ-regioselectivity is determined by the nature of the metal as well as the character of the electrophile. Our recent interest in the dimetalation of *N-tert*-butylmethacrylamide[5] and its utility as a reagent have led to an investigation of reduced versions thereof, in particular of *N,N*-dimethylmethallylamine (1).

Only few related methallylic systems have been studied previously in terms of their metalation. *O*-Methallyl carbamates[2b] and *N*-methallylcarbazole[6] apparently behave very much like regular allylic systems in that their respective lithiated equivalents react both at the α and γ carbons with no observed reaction at the methyl group. The only known example of a methallylic system in which metalation occurs at the methyl group is that of methallyl alcohol.[7] Likely reasons for the modest yields reported are the heterogeneous character of the metalation reaction and the rather weak directing potential of the carbinol function, a property which has generally been recognized

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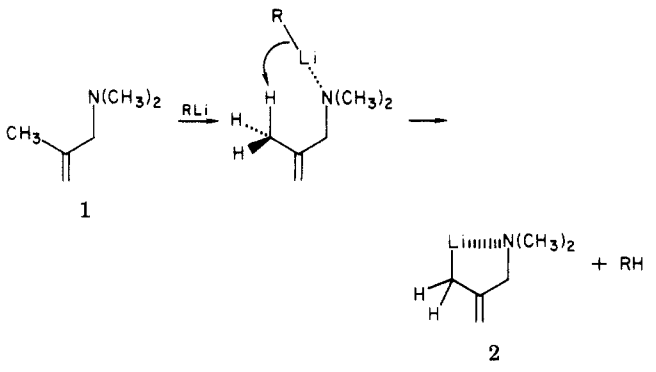
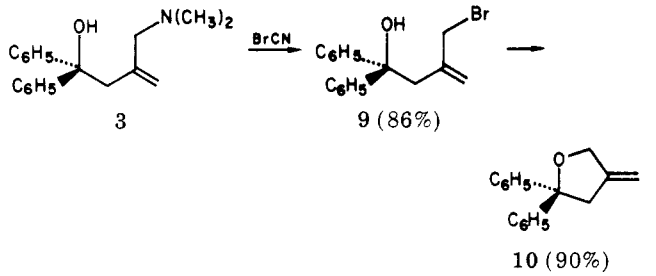
Scheme I



Scheme II



in numerous cases of ortho lithiations.[8] Tertiary aliphatic nitrogen atoms, on the other hand, have proven to be highly effective coordinating groups for the regioselective ortho functionalization of aromatic systems.[8] Furthermore, it has generally been observed that tertiary amines or diamines, such as tetramethylethylenediamine (TMEDA), markedly accelerate metalation reactions with alkyllithium reagents. This phenomenon is the result of a coordination of the nucleophilic nitrogen atom with the lithiating agent followed by its attendant depolymerization leading to an increase in the kinetic basicity.[1] Accordingly, it was assumed (Scheme I) that in *N,N*-dimethylmethallylamine (**1**) the nucleophilic nitrogen atom would serve a twofold purpose: first, coordination with the lithiating agent should enhance its kinetic basicity; secondly, in the substrate/RLi complex deprotonation should occur regioselectively at the allylic methyl group. When *N,N*-dimethylmethallylamine (**1**) is treated with *n*-butyllithium in tetrahydrofuran at 0 °C for 4 h, the allylic anion **2** is indeed formed. Upon reaction with benzophenone the expected adduct **3** can be isolated as the hydrochloride salt in 86% yield under optimal conditions. During the metalation of **1** a considerable amount of the metalating agent is consumed, most likely by the known reaction of butyllithium with tetrahydrofuran, which is accelerated by the amine.[9] Accordingly, optimal conditions employ 2 molar equiv of the readily available amine **1**, 2 equiv of metalating agent, and 1 equiv of the respective electrophile. The reaction of the anion **2** with a variety of substrates is quite general and proceeds in good to very good yields. The presence of the basic nitrogen function in the addition products is a definite advantage. In all cases, the products (**3–8**) are readily isolated as their crystalline hydrochloride salts. With the exception of product **7** in which the double bond under the experimental conditions moves into conjugation with the ketone, the terminal location of the olefin remains intact. Interestingly, products arising from reactions at the α or γ carbons (cf. **2b**, **4**, **6**) were not observed (less than 5%).

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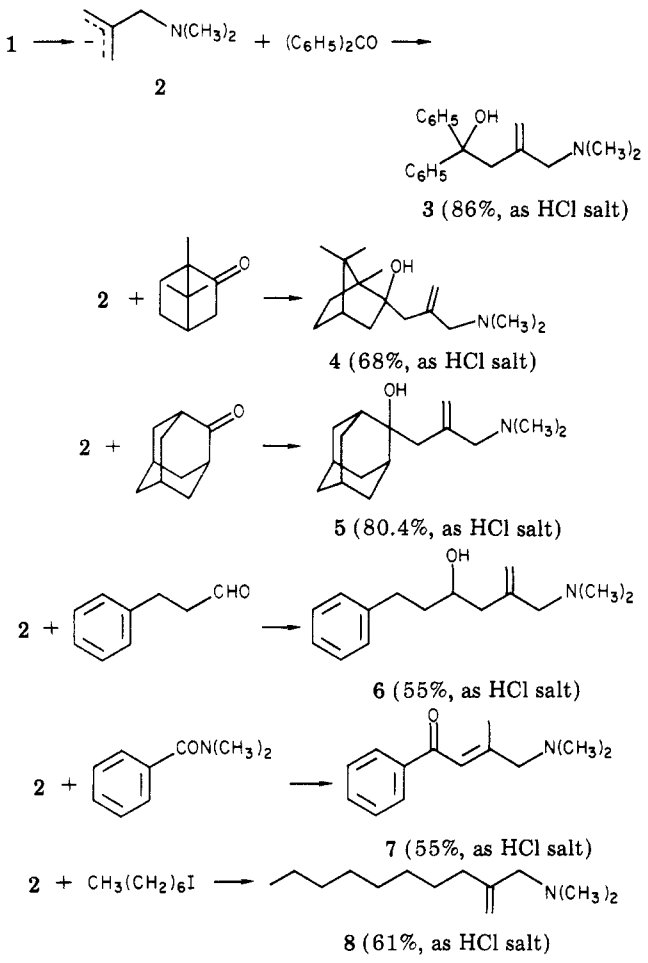
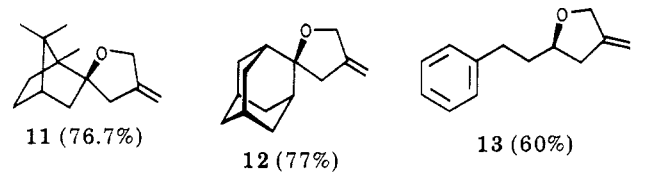


An illustration of the versatility of the allylic dimethylamino group as a functional handle for further elaboration of products **3–8** is outlined in Scheme II. The allylic bond in **3** can readily be cleaved with cyanogen bromide to produce the allylic bromide **9** in high yield. This bromide can now be used as an alkylating agent in intermolecular reactions (after protection of the carbinol) or intramolecularly as in the formation of the β-methylenetetrahydrofuran **10**. This transformation is again rather general and the overall yields of the cyclic ethers **11–13** derived from **4–6** are quite respectable.



In summary, we have described practical conditions for the efficient generation of the allylic anion **2**, derived from *N,N*-dimethylmethallylamine, which is considered a valuable synthon for the nucleophilic introduction of a functionalized, allylic four-carbon fragment. The basic character of the nitrogen atom in the products not only permits a facile isolation but also serves as a useful synthetic handle for further transformations.

Experimental Section

The physical data were obtained as follows: melting points in a Thomas-Hoover melting point apparatus (uncorrected); infrared spectra on a Perkin-Elmer 521; mass spectra on an AEI MS902 by direct insertion; proton magnetic resonance spectra on a Varian A-60, using Me_4Si as an internal standard; ^{13}C magnetic spectra on a Varian CFT-20 spectrometer. The following abbreviations are used: broad (br), weak (w), exchangeable with

D_2O (ex), singlet (s), triplet (t), quartet (q), multiplet (m).

General Procedure for Lithiation of *N,N*-Dimethylmethallylamine (1). To a stirred solution of 2.5 g (25 mmol) of *N,N*-dimethylmethallylamine (1) in 50 mL of dry THF cooled to 0 °C under a N_2 atmosphere was added dropwise 10.5 mL (25.2 mmol) of a 2.4 M solution of *N*-butyllithium in hexane. The reaction mixture was stirred for 4.0 h at 0 °C.

4-(Dimethylamino)-3-methylene-1,1-diphenylbutanol (3). To 25 mmol of allylic anion **2** prepared as described above was added a solution of 2.28 g (12.5 mmol) of benzophenone in 5.0 mL of dry THF in one portion by syringe. Stirring was continued for 15 min at 0 °C and 1.5 h at room temperature. The reaction mixture was shaken between ether and brine. The organic layer was extracted with 75.0 mL of 1 N HCl (2×). The acidic aqueous layers were basified with 2 N NaOH and extracted with methylene chloride (2 × 50 mL). The combined methylene chloride layers were dried (Na_2SO_4) and evaporated in vacuo to give **3** as an oil; NMR ($CDCl_3$) δ 2.04 (s, 6 H), 2.76 (s, 2 H), 3.17 (s, 2 H), 4.81 (s, 2 H), 7.09–7.60 (m, 10 H), 7.68 (br, 1 H, ex). A solution of this oil in acetone was treated with 1 equiv of HCl to give 3.40 g (86%) of **3** as the hydrochloride salt: mp 199–201 °C; IR (Nujol) 3290, 2610, 1635, 1590, 1040, 950, 925 cm^{-1}; mass spectrum, *m/e* 282–280 (M ± 1). Anal. Calcd for $C_{19}H_{23}NO·HCl$: C, 71.79; H, 7.61; N, 4.41. Found: C, 72.07; H, 7.91; N, 4.41.

2-[3-(Dimethylamino)-2-methylenepropyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (4). The allylic anion (25 mmol) prepared as described above was cooled to −70 °C and a solution of 1.9 g (12.5 mmol) of *dl*-camphor in 5.0 mL of dry THF was added in one portion by syringe. Stirring was continued for 15 min at −70 °C and 16 h at room temperature. The reaction mixture was worked up as previously described for compound **3** to give **4** as an oil; NMR ($CDCl_3$) δ 0.85 (s, 6 H), 1.15 (s, 3 H), 1.25–2.05 (m, 7 H), 2.17 (s, 6 H), 2.34 (s, 2 H), 2.60–3.08 (m, 2 H), 4.97 (s, 2 H), 6.47 (s, 1 H, ex). A solution of this oil in acetone–ethyl acetate was treated with 1 equiv of HCl to give 2.45 g (68%) of **4** as the hydrochloride salt: mp 207–209 °C; IR (Nujol) 3305, 2629, 1631, 1063, 942, 924 cm^{-1}. Anal. Calcd for $C_{16}H_{29}NO·HCl$: C, 66.76; H, 10.50; N, 4.87. Found: C, 65.99; H, 10.64; N, 5.28.

2-[3-(Dimethylamino)-2-methylenepropyl]adamantan-2-ol (5). The allylic anion **2** (30 mmol) prepared as described above was cooled at −70 °C and a solution of 2.25 g (15 mmol) of 2-adamantone in 10 mL of dry THF was added in one portion by syringe. Stirring was continued for 15 min at −70 °C and 16 h at room temperature. The reaction mixture was worked up as previously described for compound **3** to give **5** as a solid; NMR ($CDCl_3$) δ 1.40–1.95 (m, 8 H), 1.95–2.60 (m, 6 H), 2.18 (s, 6 H), 2.54 (s, 2 H), 2.84 (s, 2 H), 5.0 (s, 2 H), 6.8 (br, 1 H, ex). A solution of this solid in acetone–ethyl acetate was treated with 1 equiv of HCl to give 3.44 g (80.4%) of **5** as the hydrochloride salt: mp 220–223 °C; IR (Nujol) 3330, 2625, 1632, 941 cm^{-1}. Anal. Calcd for $C_{16}H_{27}NO·HCl$: C, 67.23; H, 9.87; N, 4.90. Found: C, 67.03; H, 9.88; N, 4.83.

6-(Dimethylamino)-5-methylene-1-phenylhexan-3-ol (6). The allylic anion **2** (25 mmol) prepared as described above was cooled to −70 °C and a solution of 1.67 g (12.5 mmol) of 3-phenylpropionaldehyde in 5 mL of dry THF was added in one portion by syringe. Stirring was continued for 15 min at −70 °C and 1.0 h at room temperature. The reaction mixture was worked up as previously described for compound **3** to give **6** as an oil; NMR ($CDCl_3$) δ 1.50–2.0 (m, 2 H), 2.21 (s, 6 H), 2.32 (s, 2 H), 2.50–2.93 (m, 4 H), 3.35–3.75 (m, 1 H), 4.90 (br, 2 H), 6.45 (br, 1 H, ex), 7.20 (s, 5 H). A solution of this oil in acetone–ethyl acetate was treated with 1 equiv of HCl to give 1.75 g (55%) of **6** as the hydrochloride salt: mp 105–108 °C; IR (Nujol) 3330, 2690, 1637, 1593, 1084, 932 cm^{-1}. Anal. Calcd for $C_{15}H_{23}NO·HCl$: C, 66.77; H, 8.97; N, 5.19. Found: C, 66.62; H, 9.24; N, 5.16.

4-(Dimethylamino)-3-methyl-1-phenyl-2-buten-1-one (7). The allylic anion **2** (25 mmol) prepared as described above was cooled to −70 °C and a solution of 1.86 g (12.5 mmol) of *N,N*-dimethylbenzamide in 5 mL of dry THF was added in one portion by syringe. Stirring was continued for 15 min at −70 °C and 16 h at room temperature. The reaction mixture was worked up as previously described for compound **3** to give **7** as an oil; NMR ($CDCl_3$) δ 2.14 (s, 3 H), 2.23 (s, 6 H), 2.97 (s, 2 H), 6.83–6.95 (m, 1 H), 7.19–7.55 (m, 3 H), 7.78–8.05 (m, 2 H). A solution of the oil in acetone–ether was treated with 1 equiv of HCl to give 1.64 g (55%) of **7** as the hydrochloride salt: mp 146–148 °C; IR (Nujol) 2600, 1663, 1632, 1595, 1575, 1240, 1000 cm^{-1}. Anal. Calcd for $C_{13}H_{17}NO·HCl$: C, 65.13; H, 7.57; N, 5.84. Found: C, 64.87; H, 7.70; N, 5.52.

***N,N*-Dimethyl-2-methylenedecylamine (8).** The allylic anion **2** (25 mmol) prepared as described above was cooled to −70 °C and a solution of 2.82 g (12.5 mmol) of 1-iodoheptane in 5 mL of dry THF was added in one portion by syringe. Stirring was continued for 15 min at −70 °C and 16 h at room temperature. The reaction mixture was worked up as previously described for compound **3** to give **8** as an oil; NMR ($CDCl_3$) δ 0.80–1.1 (m, 3 H), 1.15–1.65 (m, 12 H), 1.90–2.30 (m, 2 H), 2.14 (s, 6 H), 2.75 (s, 2 H), 2.81 (br s, 2 H). A solution of this oil in ethyl acetate–ether was treated with 1 equiv of fumaric acid to give 2.38 g (60.9%) of **8** as the fumarate salt: mp 80–82 °C; IR (Nujol) 1690, 1634, 1240, 1192, 972 cm^{-1}. Anal. Calcd for $C_{13}H_{27}N·C_4H_4O_4$: C, 65.14; H, 9.97; N, 4.47. Found: C, 64.95; H, 10.12; N, 4.52.

4-Methylene-2,2-diphenyltetrahydrofuran (10). To a solution of 2.81 g (10 mmol) of **3** in 50 mL of methylene chloride at 0 °C was added 10 mL of a 1.17 M solution of cyanogen bromide in methylene chloride. Stirring was continued for 15 min at 0 °C and 16 h at room temperature. The reaction was evaporated and the residue dissolved in 100 mL of ether and treated with activated charcoal (Darco). Filtration through Hy-FLO followed by evaporation in vacuo gave an oil that crystallized from ether–hexane, yielding 2.72 g (85.8%) of the allylic bromide **9**: mp 82–84 °C; NMR ($CDCl_3$) δ 2.47 (s, 1 H, ex), 3.29 (s, 2 H), 3.64 (s, 2 H), 4.90 (s, 1 H), 5.25 (s, 1 H), 7.15–7.70 (m, 10 H); IR (CH_2Cl_2) 3570, 1630, 1594, 1208, 1158, 1098 cm^{-1}. Anal. Calcd for $C_{17}H_{17}BrO$: C, 64.36; H, 5.40. Found: C, 64.42; H, 5.42.

A solution of 1.59 g (5 mmol) of this bromo alcohol in 30 mL of methylene chloride was stirred vigorously at room temperature with 15 mL of 50% NaOH and 160 mg of phase-transfer catalyst (tetrabutylammonium hydrogen sulfate). After 16 h, the methylene chloride layer was separated and evaporated. The residue was dissolved in 100 mL of ether and filtered through Hy-FLO. The filtrate was evaporated to give an oil which crystallized from hexane, yielding 1.06 g (89.8%) of compound **10**: mp 55–57 °C; NMR ($CDCl_3$) δ 3.29 (s, 2 H), 4.47 (s, 2 H), 4.78–5.18 (m, 2 H), 7.05–7.65 (m, 10 H); IR (CH_2Cl_2) 1662, 1590, 1035, 963, 877 cm^{-1}. Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.66; H, 7.02.

4-Methylenetetrahydrofuran 11. To a solution of 1.25 g (5 mmol) of allyldimethylamine **4** in 25 mL of methylene chloride at 0 °C was added 5 mL of 1.17 M solution of cyanogen bromide in methylene chloride. After 3 h at 0 °C, TLC on silica gel (developing solvent toluene) indicated all starting material had reacted, 25 mL of 50% NaOH and 200 mg of phase-transfer catalyst (tetrabutylammonium hydrogen sulfate) were added, and the reaction was stirred at room temperature. After 16 h the methylene chloride layer was separated and evaporated. The residue was taken up in 50 mL of ether and filtered through Hy-FLO. The filtrate was evaporated to give compound **11** as an oil: 790 mg (76.7%); bp 188–191 °C (14 mm); NMR ($CDCl_3$) δ 1.29 (s, 6 H), 1.61 (s, 3 H), 1.85–4.4 (complex m, 9 H), 6.45 (br s, 2 H), 7.19–7.56 (m, 2 H); IR (CH_2Cl_2) 1660, 1057, 1026 cm^{-1}; ^{13}C NMR ($CDCl_3$, one set of signals, indicating a single isomer) δ 103.5 (exocyclic methylene group), 69.3 (ring methylene group, adjacent to oxygen and unsaturation). Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.10; H, 11.11.

4-Methylenetetrahydrofuran 12. By the above procedure 1.24 g (5 mmol) of allyldimethylamine **5** gave compound **12** as an oil: 600 mg (77%); bp 94–97 °C (0.2 mm); NMR ($CDCl_3$) δ 1.5–1.95 (m, 14 H), 2.40–2.58 (m, 2 H), 4.20–4.38 (m, 2 H), 4.76–5.01 (m, 2 H). Anal. Calcd for $C_{14}H_{20}O$: C, 81.30; H, 9.87. Found: C, 80.61; H, 10.33.

4-Methylenetetrahydrofuran 13. Similarly, 1.16 g (5 mmol) of allyldimethylamine **6** gave compound **13** as an oil: 560 mg (60%); bp 92–95 °C (0.2 mm); NMR ($CDCl_3$) δ 1.64–2.97 (m, 6 H), 3.70–4.16 (m, 1 H), 4.32 (br s, 2 H), 4.81–5.12 (m, 2 H), 7.22 (s, 5 H); IR (CH_2Cl_2) 1660, 1598, 1040, 865 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 83.05; H, 8.80.

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UV), Ms. Barbara Warren (mass spectra), and Mr. G. Robertson and Mr. R. Oeckinghaus (elemental analyses).

Registry No. 1, 6000-82-4; 2, 77862-35-2; 3, 77862-36-3; 3·HCl, 77862-37-4; 4, 77862-38-5; 4·HCl, 77862-39-6; 5, 77862-40-9; 5·HCl, 77862-41-0; 6, 77862-42-1; 6·HCl, 77862-43-2; 7, 77862-44-3; 7·HCl, 77862-45-4; 8, 77862-46-5; 8 fumarate, 77862-47-6; 9, 77862-48-7; 10, 77862-49-8; 11, 77862-50-1; 12, 77862-51-2; 13, 77862-52-3.

Volume Profile of the Degenerate Equilibration of a Nonclassical 7-Norbornadienyl Cation

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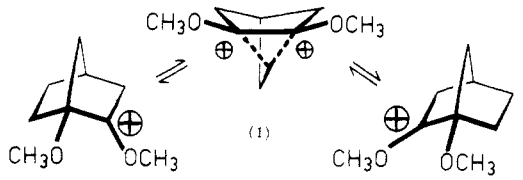
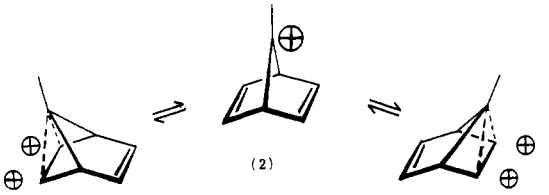
In an earlier paper,[2] we described the effect of pressure on the degenerate Wagner–Meerwein shift of the 1,2-dimethoxy-2-norbornyl cation (1). In this interconversion



of ions known to be classical,[3] symmetry demands full charge delocalization in the transition state. Since the rate of this equilibration can conveniently be determined by means of the temperature dependence of the methoxy proton magnetic resonance line shapes, use was made of our recently developed apparatus for measuring NMR spectra of solutions under pressure.[4] The volume of activation for the reaction was found to be +8 cm^3/mol, in good, if qualitative, agreement with the result expected on the grounds that charge dispersal leads to diminished solvent–ion interactions (Drude–Nernst or Born formalisms[5]) and hence to expansion. We concluded that this finding supports the validity of the use of activation volumes as a criterion for carbon participation in solvolysis,[6] at least in those cases in which the positive charge is equally distributed among at least two centers in the incipient cation.

Another interesting test of this proposal is made possible by the 7-methyl-7-norbornadienyl cation (2). In that instance, the degenerate rearrangement known as bridge flipping[7] interconverts known[8] nonclassical ions via a classical transition state; in this respect, the reaction is the exact reverse of the equilibration described above. Charge concentration now takes place as the transition state is approached; as a result of this, increased solute–solvent interaction should occur, resulting in a contraction which should reveal itself in the form of a pressure-enhanced equilibration rate.



A complication arises when the probable magnitude of this effect is appraised. The symmetry-allowed sigmatropic[9] 1,2-shift in the 2-norbornyl ion occurs without bond cleavage: the two-center 1,6 bonding pair simply becomes a three-center pair in the transition state.[10] In contrast, the three-center bond in the nonclassical 7-norbornadienyl cation is broken in the transition state, and hence this should make a positive contribution to $\Delta V^{\ddagger}$. If the charge concentration effect is gauged at −8 cm^3/mol (the opposite of the dispersal effect in the equilibration of 1) and the contribution of the breaking bond at +10 cm^3/mol,[11] one is led to anticipate a small activation volume of uncertain sign and relative indifference of the rate to the application of pressure.

We have investigated the ^1H NMR spectra of 2 in fluorosulfonic acid as a function of both temperature and pressure. The temperature-dependent spectra, while showing higher resolution than those reported by Lustgarten et al.,[12] were completely consistent with their results. At −55.4 °C, we find a clearly resolved spectrum exhibiting the bound vinyl protons at δ 7.3, the unbound vinyl protons at δ 5.9, the bridgehead protons at δ 4.9, and the methyl protons at δ 1.6. As the temperature is raised, the two vinyl proton signals broaden and finally coalesce at −16 °C; at still higher temperatures, irreversible decomposition occurs. The pressure dependence was determined at roughly 30-MPa intervals over a range of 200 MPa (~2000 atm) and at a temperature of −23 °C where broadening is already clearly visible at atmospheric pressure. As can be seen in Figure 1, the application of pressure causes no change in the NMR spectrum of 2 other than that attributable to the thermal decomposition.

The insensitivity of the bridge-flipping process of 2 to pressure is in sharp contrast to the dramatic sharpening of the methoxy signals of 1 engendered by pressure. It was pointless to simulate the spectra of 2 under pressure because all of them were superimposable except for the decomposition; however, from the sensitivity of the spectra to temperature, the resolution (estimated to be 1 Hz), the known value of $\Delta G^{\ddagger}$ (52 kJ/mol = 12.4 kcal/mol), and the expression $\Delta V^{\ddagger} = (-RT\delta \ln k)/\delta p$, it is possible to appraise the precision of our result: $\Delta V^{\ddagger} = 0 \pm \leq 3$ cm^3/mol. We conclude that, if one allows for the known effect of bond breaking, the pressure effects on the equilibration rates

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