2885, 1690, 1584, 1562, 1452, 1405, 1380, 1302, 1285, 1225, 1112, 1060 cm⁻¹; mass spectrum, m/e (relative intensity) 233 (M⁺, 86), 232 (4), 157 (11), 145 (43), 133 (24), 132 (base), 131 (50), 129 (22), 119 (22); high-resolution mass spectrum, m/e 233.1168 (C₁₂H₁₅N₃O₂ requires 233.1163).

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Attempted Cyclization of an Epoxide. Elimination of an Epoxide

Irvin Rothberg,* Louis Schneider, Sheldon Kirsch, and Robert OFee

Olson Laboratories, Department of Chemistry, Rutgers, The State University of New Jersey, Newark, New Jersey 07102

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The cyclization of halo epoxides treated with lithium has been reported previously.^{1,2} We attempted the transformation of chloro epoxide 1 into tetracyclic alcohol 2 using an analogous procedure. However, tetracyclic alcohol 2 was prepared in only 3% yield (GLC). The major product, found in 60% yield (GLC), was *endo*-4-methyl*syn*-tricyclo[5.2.1.0^{2,6}]dec-8-ene (3).



Perhaps there are steric interactions between the methylene group and the hydrogens of the epoxide ring so that cyclization is slowed. Other reactions then take place. To examine further the geometric requirements for ring closure to occur, we reacted the chloro epoxide derivative of a straight-chain hydrocarbon with lithium. 1,2-Epoxy-6-chlorohexane (4) was reacted with lithium in



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Scheme I



tetrahydrofuran. GLC examination of the products showed a complex mixture of 15 different compounds. None was present as a major component. There was no cyclohexanol or cyclopentylmethanol produced, which would have been the expected cyclization products. Clearly, for cyclization to occur there are very severe restrictions on the geometry of the chloro epoxide.

We investigated whether the chloromethylene group must be present for reductive epoxide removal to occur. 2,3-Epoxynorbornane (5) was treated with lithium to yield 60% exo-norborneol and 1% norbornene (GLC). It was recognized that lithium chloride was generated when chloro epoxide 1 was treated with lithium. It had been previously reported that a mixture of magnesium amalgam and magnesium bromide led to reductive eliminations of epoxides.³ We wanted to see if lithium mixed with lithium chloride was responsible for the elimination occurring in the reaction of 1 with lithium. Consequently, we treated 5 with lithium in tetrahydrofuran containing lithium chloride in a 1:2.5 molar ratio of epoxide to halide. This led to a 64% yield of exo-norborneol and 3% of norbornene (GLC). The presence of lithium chloride is not leading to elimination.

For elimination to occur in major amounts, the chloromethyl group must be present. A reasonable mechanism which accounts for the experimental facts is shown in Scheme I. The development of a relatively unstable trianionic intermediate, **6**, where the negative charges repel each other, would trigger an elimination. The major product resulting from the reaction of 2,3-epoxynorbornane with lithium is *exo*-norborneol. In this case dianionic intermediate 7 is produced. Repulsions are less, and the intermediate 7 is sufficiently stable that it does not eliminate and subsequently is protonated to produce an alcohol. Dianionic intermediate 7 is similar to those suggested by Kaiser and co-workers,⁴ who studied the reaction of epoxides with alkali metals in liquid ammonia.

The reaction of steroidal epoxides with lithium in ethylamine has been studied.⁵ It has been reported for steroidal epoxides that if a hydroxyl group is in the vicinity of the epoxide, substantial reductive elimination takes place. Mechanistic details were not reported in that study. It seems very likely that an elimination occurred for reasons similar to those suggested for halo epoxide 1. A

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trianionic intermediate forms which rapidly eliminates.



Chloro epoxide 1 was prepared from compound $8^{2,6}$ as outlined. All spectral data were in agreement with the structures shown.



Ketone $8^{2,6}$ was treated with methylenetriphenylphosphorane to produce diene 9 in 69% yield. Diene 9 was reacted with disiamylborane and the product oxidized to yield alcohol 10 in 60% yield. The alcohol was assigned the configuration shown, rather than the epimeric configuration, for several reasons. Attack of disiamylborane should be from the less hindered side of the methylene group to yield alcohol 10. It has been shown previously that attack of lithium aluminum hydride on 8 produces the endo alcohol exclusively.^{2,6} This is in agreement with the direction of attack proposed for the reaction of disiamylborane with the methylene derivative. Also, preparation of the tosylate derivative of 10 followed by acetolysis and saponification of the resulting acetate led to a 35% yield of alcohol 2. This could only be produced by participation of the double bond with an endo-methylene cation.

Treatment of alcohol 10 with thionyl chloride gave chloroalkene (65% yield), which when treated with m-chloroperoxybenzoic acid led to epoxide 1 in 82% yield.

Experimental Section

Melting points were determined with a Thomas-Hoover apparatus and are uncorrected. IR spectra were recorded on a Beckman IR-10 instrument. ¹H NMR spectra were determined on a Varian XL-100 spectrometer with deuteriochloroform as the solvent and with tetramethylsilane as an internal standard. Mass spectra and GC/MS were determined on an AEI MS 30 instrument at 70 eV.

4-Methylene-syn-tricyclo[5.2.1.0^{2,6}]dec-8-ene (9). Ketone $8^{2.6}$ (20.1 g, 0.134 mol) was treated with methylenetriphenylphosphorane essentially according to the Corey procedure⁷ and the product distilled to give 13.7 g (69%) of an oil which was analytically pure: bp 72–74 °C (9 mm); IR (film) 3070, 1660, 860 cm⁻¹; ¹H NMR δ 6.08 (m, 2 H), 4.55 (m, 2 H), 2.80 (m, 4 H), 2.3–1.2 (complex m, 6 H); mass spectrum, m/e (relative intensity) 146 (18, M⁺), 117 (5), 91 (11), 80 (87), 66 (100). Anal. Calcd for C₁₁H₁₄: C, 90.34; H, 9.66, Found; C, 90.32; H, 9.42.

endo-4-(Hydroxymethyl)-syn-tricyclo[5.2.1.0^{2,6}]dec-8-ene (10). Olefin 9 (13.7 g, 0.0937 mol) was treated with disiamylborane by utilizing essentially the procedure of Brown and Zweifel.⁸ After the workup the alcohol was distilled to give 9.3 g (60%) of an oily analytical sample: bp 89-91 °C (0.6 mm); IR (liquid film) 3350, 3070, 2960, 2870, 1060 cm⁻¹; ¹H NMR δ 6.13 (s, 2 H), 3.41 (d, J = 6 Hz, 2 H), 3.12 (s, 1 H, OH), 2.70 (m, 4 H), 2.3-1.0 (complex m, 5 H), 1.0-0.2 (complex m, 2 H); mass spectrum, m/e (relative intensity) 164 (25, M⁺), 146 (28), 105 (15), 92 (18), 91 (27), 80 (58), 66 (100). Anal. Calcd for C₁₁H₁₆O: C, 80.44; H, 9.82. Found: C, 80.30; H, 9.96. endo-4-(Chloromethyl)-syn-tricyclo[5.2.1.0^{2,6}]dec-8-ene (11). Alcohol 10 (1.19 g, 7.24 mmol) was dissolved in 2.5 mL of benzene, and 1.18 g of thionyl chloride in benzene was added at 25 °C. The reaction mixture was then refluxed for 4 h. GLC analysis indicated the alcohol was completely converted to chloride. The reaction mixture was worked up in the usual way and the crude product distilled to give 0.871 g (65%) of oily analytically pure product: bp 77-80 °C (1.0 mm); IR (liquid film) 3050, 2950, 2860, 725 cm⁻¹; ¹H NMR δ 6.15 (s, 2 H), 3.36 (d, J = 6 Hz, 2 H), 2.70 (m, 4 H) 2.5-1.1 (complex m, 5 H), 1.1-0.3 (complex m, 2 H). Anal. Calcd for C₁₁H₁₆Cl: C, 71.92; H, 8.78; Cl, 19.30. Found: C, 72.15; H, 8.60; Cl, 18.96.

exo-8,9-Epoxy-endo-4-(chloromethyl)-syn-tricyclo-[5.2.1.0^{2,6}]decane (1). Chloroalkene 11 (0.410 g, 2.24 mmol) was dissolved in 2.5 mL of dichloromethane. To this was added 0.750 g of 85% m-chloroperoxybenzoic acid in dichloromethane and the mixture refluxed for 4 h. The mixture was diluted with dichloromethane, extracted with 20% sodium sulfite, and then worked up in the usual way. The crude product, after rotary evaporation of solvent, was distilled to give 0.364 g (82%) of an oily analytical sample: bp 89–90 °C (0.2 mm); IR (liquid film) 840, 710 cm⁻¹; ¹H NMR δ 3.50 (d, J = 6 Hz, 2 H), 3.26 (s, 2 H), 2.40 (m, 4 H), 2.0–0.85 (complex m, 7 H); mass spectrum, m/e(relative intensity) 198 (5, M⁺), 169 (23), 163 (22), 131 (100), 105 (21), 93 (30). Anal. Calcd for C₁₁H₁₅ClO: C, 66.49; H, 7.61; Cl, 17.85. Found: C, 66.47; H, 7.78; Cl, 18.19. **Reaction of 1 with Lithium. Preparation of endo-4**-

Reaction of 1 with Lithium. Preparation of endo-4-Methyl-syn-tricyclo[5.2.1.0^{2,6}]dec-8-ene (3). Tetrahydrofuran (2 mL) and 0.310 g of a 50% lithium dispersion in pentane were added to a 5-mL flask. A solution of 0.216 g (1.08 mmol) of 1 in 2 mL of tetrahydrofuran was added, and the reaction mixture, under a static pressure of helium, was refluxed with vigorous stirring for 48 h. The workup was carried out essentially as described previously² to give a 60% yield of 3 (GLC with an external standard). An oily analytical sample was obtained by preparative GLC: IR (liquid film) 3060, 2955, 2860, 718 cm⁻¹; ¹H NMR δ 6.07 (s, 2 H), 2.68 (m, 4 H), 2.2–1.0 (complex m, 7 H), 0.90 (d, J = 6 Hz, 3 H). Anal. Calcd for C₁₁H₁₆: C, 89.12; H, 10.88. Found: C, 88.79; H, 11.14.

Reaction of 2,3-Epoxynorbornane with Lithium. A solution of 5 in tetrahydrofuran was treated with lithium dispersion in essentially the same manner as described for the reaction of 1 with lithium. After the workup, GLC indicated a 60% yield of *exo*-norborneol and 1% of norbornene. In addition, 31% of unreacted 5 was present.

Reaction of 5 with Lithium and Lithium Chloride. The reaction conditions were the same as described previously with the exception that lithium chloride was added and was present in a 1:2.5 molar ratio of epoxide to lithium chloride. After the work, GLC indicated a 64% yield of *exo*-norborneol, 3% of norbornene, and 32% of unreacted 5. The products of the reaction were identical with authentic materials when compared by GC/MS.

1,2-Epoxy-6-chlorohexane (4). *m*-Chloroperoxybenzoic acid (85%, 5.0 g) was added to a carbon tetrachloride solution containing 2.11 g (17.8 mmol) of 6-chloro-1-hexene kept at 5-10 °C. The reaction mixture was stirred for 1 h at this temperature and then was stirred for 20 h at room temperature. The solution was extracted with sodium sulfite and then worked up in the usual way. After evaporation of the solvent, the crude chloro epoxide was distilled to give 1.85 g (77%) of epoxide: bp 67-68 °C (7.5 mm); IR (liquid film) 2930, 2855, 820, 630 cm⁻¹; ¹H NMR δ 3.52 (t, J = 6 Hz, 2 H), 2.71 (m, 2 H), 2.5-2.3 (m, 1 H), 1.64 (complex m, 6 H). Anal. Calcd for C_eH₁₁ClO: C, 53.53; H, 8.24; Cl, 26.35. Found: C, 53.52; H, 8.01; Cl, 26.20.

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Registry No. 1, 81724-51-8; **2**, 81724-52-9; **2** tosylate, 81724-53-0; **2** acetate, 81724-54-1; **3**, 81724-55-2; **4**, 81724-56-3; **5**, 3146-39-2; **8**, 51176-00-2; **9**, 81724-57-4; **10**, 81724-58-5; **11**, 81724-59-6; 6-chloro-**1**-hexene, 928-89-2.