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Friedel-Crafts Cyclialkylations of Some Epoxides

Stephen K. Taylor,* Gregory H. Hockerman, Gregory L. Karrick, Stephen B. Lyle, and Scott B. Schramm

Department of Chemistry, Olivet Nazarene College, Kankakee, Illinois 60901

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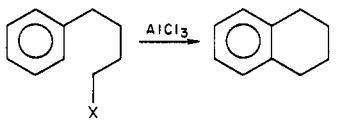
Several arylalkyl epoxides (1–9) were investigated for cyclialkylation reactions. Cyclialkylation to form six-membered rings was observed (up to 91% isolated yields) at secondary but not at primary epoxide positions. Cyclialkylation was not observed with 4-phenyl-1,2-epoxybutane, but a *m*-methoxy substituent did promote ring closure to the primary position in moderate yield. Cyclialkylation to seven-membered rings occurred at a secondary position in reasonable yields; less rearrangement occurred with the epoxide system than with analogous alkylating agents such as phenylalkyl alcohols. Reduced skeletal rearrangement is characteristic of cyclization reactions that occur with epoxides and suggests that the epoxide serves to moderate electrophilic reactivity. Cyclialkylation to form five-membered rings was not observed with epoxides that were capable of ring-opening at primary or secondary positions.

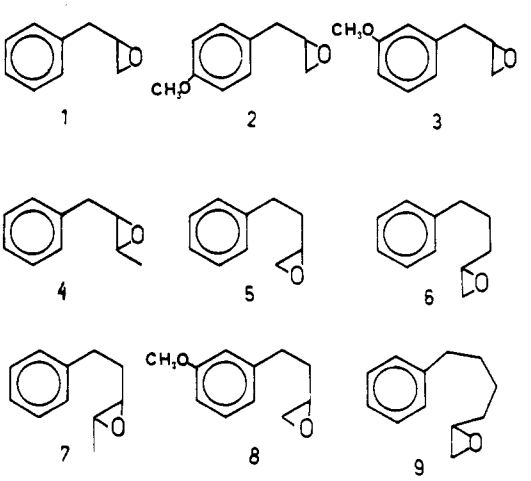
Numerous excellent reports on polyene cyclizations have appeared in the literature.[1-5] A simpler variant of this chemistry is the intramolecular cyclialkylation[6,7] reaction (eq 1) in which ring closure occurs to an aromatic group



(1)

via a previously functionalized position of an alkyl side chain.[8] This Friedel–Crafts chemistry provides a novel method of ring formation and has been useful in the synthesis of natural and medicinal compounds.[9,10] Although

Chart I

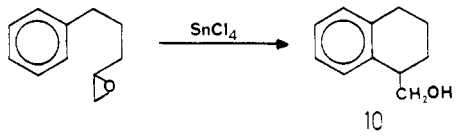


cyclialkylation reactions have been investigated thoroughly[7] for arylalkyl halides,[11,12] olefins,[13,14] and alcohols,[11a,13,15,16] only one investigation has been reported on comparable epoxide cyclialkylations.[17]

(1) van Tamelen, E. E. *Acc. Chem. Res.* **1975**, *8*, 152 and references therein.
(2) Johnson, W. S. *Bioorg. Chem.* **1976**, *5*, 51.
(3) (a) van Tamelen, E. E.; Loughhead, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 869. (b) van Tamelen, E. E.; Freed, J. H. *Ibid.* **1970**, *92*, 7202, 7206.
(4) (a) Goldsmith, D. J. *J. Am. Chem. Soc.* **1962**, *84*, 3913. (b) Goldsmith, D. J.; Cheer, C. J. *J. Org. Chem.* **1965**, *30*, 2264.
(5) Harding, K. E.; Cooper, J. L.; Puckett, P. M. *J. Org. Chem.* **1979**, *44*, 2834.
(6) Bruson, H. A.; Kroeger, J. W. *J. Am. Chem. Soc.* **1940**, *62*, 36.
(7) Olah, G. A. "Friedel–Crafts Chemistry"; Wiley-Interscience: New York, 1973; pp 59–62, 185–186.
(8) Recently, a polyene cyclization was reported that involves cyclization to an aromatic group. It is an olefinic position that becomes attached to the aromatic group, not the epoxide as in our studies. See: van Tamelen, E. E.; Carlson, J. G.; Russel, R. K.; Zawacky, S. R. *J. Am. Chem. Soc.* **1981**, *103*, 4615. The alkylation of an olefin is more facile than the alkylation of an aromatic because the loss of aromaticity in the transition state is unfavorable (see ref 7, p 533).
(9) Ireland, R. E.; Baldwin, S. W.; Welch, S. C. *J. Am. Chem. Soc.* **1972**, *94*, 2056.
(10) Mendelson, W. L.; Spainhour, C. B., Jr.; Jones, S. S.; Lam, B. L.; Wert, K. L. *Tetrahedron Lett.* **1980**, *21*, 1393.
(11) (a) Khalaf, A. A.; Roberts, R. M. *J. Org. Chem.* **1972**, *37*, 4227. (b) *Ibid.* **1966**, *31*, 89.
(12) Mihel, I.; Orlović, M.; Polla, E.; Borčić, S. *J. Org. Chem.* **1979**, *44*, 4086.
(13) (a) Bogert, M. T.; Davidson, D. *J. Am. Chem. Soc.* **1934**, *56*, 185. (b) *Ibid.* **1935**, *57*, 151.
(14) Tolbert, L. M. *J. Org. Chem.* **1979**, *44*, 4584.
(15) Khalaf, A. A.; Roberts, R. M. *J. Org. Chem.* **1969**, *34*, 3571.
(16) Colonge, J.; Weinstein, G. *Bull. Soc. Chim. Fr.* **1952**, 462.
(17) Davidson, A. J.; Norman, R. O. C. *J. Chem. Soc.* **1964**, 5404.

0022-3263/83/1948-2449$01.50/0

Scheme I



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Epoxides have an added dimension over the other functional groups studied:[11-16] they can ring open in either of two directions. Also, the products resulting from these cyclialkylations would have a useful functional group (hydroxyl) two carbons removed from the aromatic ring, in contrast to other reactions.[11-16]

Earlier, we reported the investigation of the highly stereoselective intermolecular Friedel–Crafts epoxide cyclization reaction of *trans*-5,6-epoxy-*cis*-cyclodecene with stannic chloride.[18] This investigation prompted us to investigate selectivity in intramolecular cyclization reactions on epoxides **1–9** (Chart I) and compare their behavior with that of the alcohols and halides studied earlier.[11-16] We now report the versatility of epoxide cyclization reactions relative to that of previously investigated systems.

The epoxides (**1–9**, Chart I) were synthesized by preparation of an olefin from an allylic halide and a suitable Grignard reagent ($Ar(CH_2)_3MgBr$ + $R'CH{=}CRCH_2X$) followed by epoxidation with *m*-chloroperoxybenzoic acid (MCPBA) or cyclization of a bromohydrin[19] made from the olefin. They were chosen to determine if cyclialkylation occurs at primary and secondary positions to form five-membered (**1–5**), six-membered (**5–8**), and seven-membered (**6**, **9**) rings.

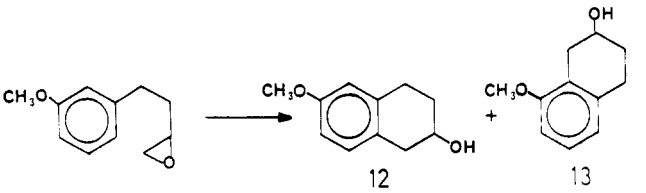
Results and Discussion

Since other workers[11,13,15] have shown that six-membered-ring cyclialkylation (6-MRC) is favored over that of five- and seven-membered, we expended considerable effort trying to develop an optimum cyclization method for the formation of six-membered-ring systems. We have also investigated these reactions in a nonpolar solvent as did Khalaf and Roberts[11,15] so our comparisons with other systems would be valid. Our Friedel–Crafts (FC) reactions are performed in dilute solutions to minimize polymerization and other intermolecular reactions.[18]

Epoxide **6** undergoes high yield (91%) 6-MRC (Scheme I), showing that these reactions are of good synthetic potential. The 6-MRC occurs when heptane or dichloromethane solvents are used, with TFA, boron trifluoride etherate, and stannic chloride as Lewis-acid promoters. However, best yields were obtained by treatment of **6** with 2 equiv of $SnCl_4$ in dichloromethane. The identity of the product was proven by comparison with physical constants and derivative melting points of authentic 1,2,3,4-tetrahydro-1-naphthalenemethanol[20,21] (**10**) as well as by spectral analysis. A yield of 85% is obtained by using $SnCl_4$ in heptane, a hydrocarbon solvent like that employed by Khalaf and Roberts.[11,15]

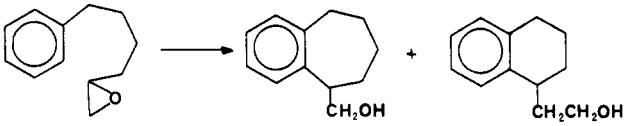
6-MRC was also observed for 2,3-epoxy-5-phenylpentane (**7**). It cyclizes to 1-methyl-1,2,3,4-tetrahydro-2-naphthol[22] (**11**) in 57% yield. The noncyclized products of all our epoxide reactions formed from similar pathways and are therefore generalized at the end of this paper. The analysis of the products of this reaction using 11 different GC columns failed to detect isomers from 5-MRC.

Scheme II



12 13

Scheme III



Despite many attempts at ring-closing **5**, cyclization was never achieved. This was shown by GC, NMR, and IR comparison with an authentic sample of 1,2,3,4-tetrahydro-2-naphthol, the expected product.[17] Conditions used in our attempts were to treat 1,2-epoxy-4-phenylbutane with 1 equiv or more of $AlCl_3$ in nitromethane, carbon disulfide, or benzene: also, $SnCl_4$ in heptane or benzene, SbF_5 in dichloromethane at low temperatures, and polyphosphoric acid[9] failed to cyclize the epoxide. This lack of intramolecular alkylation corroborates an earlier limited study on **5** by Norman and Davidson[17] using trifluoroacetic acid (TFA) in dichloromethane.

Both studies indicate that 6-MRC at primary epoxide positions and 5-MRC at secondary centers[23] are not facile. In comparison with the cyclialkylation of alcohols and halides, the former is consistent but the latter is not.[11,13,15] For example, 4-phenyl-1-butanol gives a 50% cyclization yield[15] (1,2,3,4-tetrahydronaphthalene) whereas epoxide **5** gives less than 1%. But in these same studies, 5-MRC at primary and secondary positions did not occur either.

The methoxy substituent on **8** definitely promoted 6-MRC as 18% and 30% cyclialkylation yields were obtained by using $SnCl_4$/heptane and $SnCl_4/CH_2Cl_2$, respectively. However, contrary to an earlier report[17] in which TFA/CH_2Cl_2 conditions were used, we observed ortho alkylation (Scheme II, **12**) in addition to the reported para alkylation (Scheme II, **13**) in a 29:71 ratio. To clear up this discrepancy, we have repeated the earlier work. When **8** is treated with an excess of TFA in CH_2Cl_2 for 2 h and the resulting TFA esters are hydrolyzed with methanolic HCl, 18–30% of the products result from cyclization, with the remaining product being 4-*m*-anisylbutane-1,2-diol.[17] Basic hydrolysis of the esters also gives the same results. Still we found both ortho and para alkylation products in a 23:77 ratio. However, when repeating the earlier VPC analysis of the product mixture, we were also unable to cleanly separate **12** and **13**.[25] However, an FFAP column cleanly separated these compounds, and they were unambiguously identified (see Experimental Section) following preparative GC. Hence, the earlier workers[17] apparently overlooked the ortho product because optimum VPC analysis conditions were not used. Also, in a control ex-

(18) Taylor, S. K.; Lilley, G. L.; Lilley, K. J.; McCoy, P. A. *J. Org. Chem.* **1981**, *46*, 2709 (see references therein for general information on epoxide FC reactions).

(19) Guss, C. O.; Rosenthal, R. *J. Am. Chem. Soc.* **1955**, *77*, 2549. This method cannot be used with methoxy-substituted aromatics as some ring bromination occurs.

(20) Huisgen, R.; Seidl, G. *Chem. Ber.* **1963**, *96*, 2740.

(21) Newman, M. S.; O'Leary, T. J. *J. Am. Chem. Soc.* **1946**, *68*, 258.

(22) The complex NMR multiplet of the CH–O proton suggests the methyl and hydroxyl groups are in a trans configuration (predominantly equatorial,equatorial). We are currently synthesizing both geometric isomers to verify this.

(23) 1-(Hydroxymethyl)indan did not form either. For data on this compound, see: Huisgen, R.; Laschturvka, E.; Ugi, I.; Kammermeier, A. *Justus Liebigs Ann. Chem.* **1960**, *630*, 128.

(24) We found that up to 30% cyclization products can be obtained.

(25) If a slow carrier gas flow rate was used, a peak shoulder was observed, but no separation was observed at high flow rates.

periment, it was shown that **12** did not rearrange to **13** under the reaction conditions.

We found a dramatic difference in epoxide 7-MRC (of **9**) vs. other alkylating agents. In a simple phenylalkyl alcohol capable of 7-MRC, rearrangement completely took place to give 6-MRC, even though this required a tertiary-to-secondary carbocation rearrangement.[11a] In contrast, 7-MRC of an epoxide was more facile: treatment of **9** with $SnCl_4$ in dichloromethane gives two cyclialkylation products in a combined 65% yield (Scheme III). The same reaction in heptane gives only 18% yield of **14** and **15**.

We did observe some rearrangement to a six-membered ring, but not to the extent observed with other substrates:[11] the ratio of 7-MRC to 6-MRC (**14**:**15**) was 77:23. Hence, the reaction was fairly selective and differed significantly from work with alcohols.

In contrast to the successful 6-MRC reactions described above, none of the epoxides capable of undergoing 5-MRC (**1**–**5**) did. Again, several different conditions were used in our attempts (vide supra). However, a comparable lack of 5-MRC was reported in work on primary and secondary arylalkyl halides and alcohols.[11,15] Hence, epoxides do not behave as though they are more electrophilic than other alkylating agents: indeed they appear less so in the attempts at 6-MRC at primary epoxide positions.

We believe the slightly reduced electrophilicity of epoxides in these (and other[18]) Friedel–Crafts reactions and the increased selectivity (reduced rearrangement) can be attributed to oxygen bridging in the transition state.[26] This could amount to a push–pull mechanism, which has been demonstrated in many epoxide reactions,[27] where bond breaking leads to bond making. When compared to other electrophiles, the cationic character of the electrophilic carbon is thereby reduced by a partial bond to the oxygen. However, this bridging also reduces cationic rearrangements compared to other functional groups. Indeed, the alkylation of benzene by methyloxirane has been reported to give 100% inversion,[28] in agreement with our contention.

Although the exact mechanistic interpretation of these reactions may be subject to debate and various mechanistic viewpoints, we would like to point out a practical uniqueness of epoxide FC reactions: The epoxide acts in principle as its own neighboring group. Regardless of whether the reaction goes via an ion pair, a concerted, or nonconcerted mechanism, etc., the epoxide is unique because special stereochemistry[28] or regiospecificity results as a consequence of the epoxide oxygen stabilizing an intermediate or transition state by partial bonding to the reaction center. The epoxide is the reaction center and the neighboring group;[29,30] and although a saturated epoxide FC reaction is known to give inversion and can be considered an S_N2-like reaction[28] (as can neighboring-group epoxide formation), the transition state resembles a neighboring-group reaction more.

The side products of all the reactions can be generalized. Rearrangement of the epoxide to give a carbonyl compound, formation of a chlorohydrin and formation of a diol (from attack of acidic water on the unaltered epoxide during workup) were the major side products. As an example, when 1,2-epoxy-5-phenylpentane (**6**) was treated with $SnCl_4$ in heptane and stirred for 23 h, the product distribution after workup was 5% 5-phenylpentanal, 85% **10**, 4% 2-chloro-1-hydroxy-5-phenylpentane, and 6% 5-phenylpentane-1,2-diol. If low or 0% cyclialkylation yields were obtained, proportionately more carbonyl, chlorohydrin, and diol compounds were obtained. For example, when **4** was treated as above, 4-phenyl-2-butanone, 4-phenyl-3-butanone, an unknown compound, two chlorohydrins, and 4-phenylbutane-2,3-diol resulted in a 15:8:9:35:33 ratio. This was shown by GC–MS and NMR and IR analysis on samples isolated by preparative VPC.

The presence of chlorohydrin in the reaction mixture brings up another possible source of cyclization: a chlorohydrin may form from the epoxide and subsequently undergo cyclialkylation.[31] To see if that is the source of our cyclialkylation products, we prepared the chlorohydrin $PhCH_2CH_2CH_2CHClCH_2OH$ from epoxide **6** by a general method[32] and treated it with $SnCl_4$ under the Friedel–Crafts cyclization conditions. However, the chlorohydrin was recovered essentially unchanged, showing that this route is not the pathway to the products we observe.

Experimental Section

Infrared spectra were obtained on Perkin-Elmer 137 and Beckman IR10 spectrophotometers. GC analyses were performed on Varian A90-P3 and Hewlett-Packard 5712 TC detector instruments using a 10-ft 5% SE-30 or 6-ft 5% FFAP column and a Hewlett-Packard 3380 A integrator–recorder. Routine NMR spectra were recorded on a Varian EM 360A spectrometer. MS data were obtained on VG MM16 and 70–70 instruments. Melting points are uncorrected and were obtained on a Mel-Temp apparatus. Elemental analyses were determined by Galbraith Labs., Inc. The syntheses of epoxides **1**,[33] **5**,[17,34] **6**,[34] **8**,[17] and **9**[34] have been reported. All chemicals were used in reagent purity unless otherwise noted. Heptane was dried over sodium, and CH_2Cl_2 was distilled from P_2O_5 immediately before use. All glassware was dried before use.

General Epoxidation Procedure.[35] A solution of 0.1 mol of *m*-chloroperoxybenzoic acid and 250 mL of $CHCl_3$ was added over 90 min to 0.1 mol of alkene in 250 mL of $CHCl_3$. After 6 h of reflux, 200 mL of petroleum ether was added, the solution was cooled, and the precipitated *m*-chlorobenzoic acid was filtered off. The filtrate was washed twice with 20% $NaHSO_3$, three times with 5% $NaHCO_3$, and once with 10% NaCl. The dried ($MgSO_4$) organic layer was concentrated and distilled to obtain pure epoxide (50–80% isolated yields).

1,2-Epoxy-3-(*m*-methoxyphenyl)propane (3).[36] The compound was prepared as described in the discussion section: bp 148–150 °C (7.8 mm); n^{25}_D 1.5286; ^1H NMR (CCl_4) δ 2.3–3.2 (m, 5 H), 3.7 (s, CH_3O), 6.4–7.4 (m, 4 H, Ar H); IR (AgCl disks) 1250 (ether), 830, 770, and 690 (meta) cm^{-1}.

2,3-Epoxy-1-phenylbutane (4).[36] **4** was distilled from the Grignard product epoxidation procedure as a mixture of cis and trans isomers: bp 83–84 °C (4.6 mm); n^{25}_D 1.5080; ^1H NMR (CCl_4)

(26) This can also be explained by a concerted reaction. However, both these explanations can be equivalent, depending on one's mechanistic viewpoint on ion pairs.

(27) Parker, R. E.; Isaacs, N. S. *Chem. Rev.* **1959**, *59*, 737.

(28) Nakajima, T.; Suga, S.; Sugita, T.; Ichikawa, K. *Tetrahedron* **1969**, *25*, 1807.

(29) Noller, C. R. "Chemistry of Organic Compounds", 3rd. ed.; Saunders: Philadelphia, PA, 1965; p 821. Although textbooks vary in their definition of neighboring-group effects, we are using Noller's definition (for α substituents) as the stabilization of an intermediate or transition state by bonding partially to the reaction center.

(30) (a) Isaacs, N. S. "Reactive Intermediates in Organic Chemistry"; Wiley: New York, 1974; p 207. (b) Hine, J. "Physical Organic Chemistry"; McGraw-Hill: New York, 1962; p 144. (c) Breslow, R. "Organic Reaction Mechanisms"; W. A. Benjamin: New York, 1966; p 73.

(31) For an example of a halohydrin FC alkylation, see: Bachman, G. B.; Hellman, H. M. *J. Am. Chem. Soc.* **1948**, *70*, 1772.

(32) VanderWerf, C. A.; Stewart, C. A. *J. Am. Chem. Soc.* **1954**, *76*, 1259.

(33) Chapman, N. B.; Isaacs, N. S.; Parker, R. E. *J. Chem. Soc.* **1959**, 1925.

(34) Lévy, J.; Sfiras, J. *Bull. Soc. Chim. Fr.* **1931**, *49*, 1823.

(35) Paquette, L. A.; Barrett, J. H. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, p 467.

(36) Adequate combustion (±0.4%) or HRMS analyses were obtained for these compounds.

δ 1.2 (d, 3 H, J = 6 Hz), 2.4–3.1 (m, 4 H), 7.2 (s, 5 An H); IR (AgCl disks) 860, 730, and 690 (monosubstituted benzene) cm^{-1}.

2,3-Epoxy-5-phenylpentane (7).[36] Epoxidation of the precursor (predominantly trans[37]) gave the epoxide: bp 70–71 °C (0.75 mm); n^{25}_D 1.5044; ^1H NMR (CCl_4) δ 1.1 (d, 3 H, J = 5 Hz), 1.8 (m, 2 H), 2.6 (m, 4 H), 7.1 (s, 5 Ar H); IR (AgCl disks) 860, 740, and 690 (monosubstituted benzene) cm^{-1}.

General Friedel–Crafts Cyclialkylation Procedure. A solution of 6 mmol of epoxide in 8 mL of dry CH_2Cl_2 (or heptane) was added over 10 min to 12 mmol of Lewis acid (usually $SnCl_4$) in 80 mL of dry CH_2Cl_2 (or heptane). After 4 h of reflux, the mixture was stirred at room temperature for 19 h and then added to an equal volume of ice water. After addition of 80 mL of ether, the organic layer was washed with 5% $NaHCO_3$ and 15% NaCl and dried ($MgSO_4$). After evaporation of the solvents, the compounds were analyzed by GC, NMR, and IR spectroscopy.

1,2,3,4-Tetrahydro-1-naphthalenemethanol (10). Cyclization of 2.00 g of **6** in hexane by the above method (double scale) gave 2.0 g of product that was 85% (85% yield) **10**, 5% 5-phenylpentanal, 4% 2-chloro-5-phenyl-1-pentanol, and 6% 5-phenylpentane-1,2-diol. Short-path distillation gave 1.6 g of **10**: bp 113–117 °C (1.2 mm), n^{22}_D 1.5528 [lit.[20,38] bp 114–118 °C (1 mm), n^{22}_D 1.5616]; ^1H NMR ($CDCl_3$) δ 1.3–2.1 (m, 4 H), 2.3–3.2 (m, 4 H), 3.7 (d, 2 H, J = 6.5 Hz), 7.1 (m, 4 Ar H); IR (AgCl disks) 3200–3600 (br, OH), 1040 (OH), 750 (d, ortho) cm^{-1}. Phenyl- and naphthylurethane derivatives melting points were 99–100 °C (lit.[20] mp 97.5–98.5 °C) and 123–125 °C (lit.[38] mp 125.4–126.2 °C). The same reaction conducted in CH_2Cl_2 gave the alcohol in 91% yield.

1-Methyl-1,2,3,4-tetrahydro-2-naphthol (11).[36] Cyclization of **7** gives **11**[22] in 57% distilled yield: bp 99–101 °C (0.18 mm), n^{25}_D 1.5501 [lit.[39] bp 105–107 °C (0.2 mm), n^{25}_D 1.5570]; ^1H NMR (CCl_4) δ 1.2 (d, 3 H, J = 7 Hz), 1.5–2.1 (m, 2 H), 2.3–2.9 (m, 3 H), 3.1 (s, 1 OH), 3.6 (m, CH–O), 7.0 (m, 4 Ar H); IR (AgCl disks) 3200–3600 (OH), 1030 (OH), 755 (ortho) cm^{-1}.

6-Methoxy-1,2,3,4-tetrahydro-2-naphthol (12) and 8-Methoxy-1,2,3,4-tetrahydro-2-naphthol (13). The Friedel–Crafts procedure with **8** in CH_2Cl_2 gave products in the following ratios (FFAP column, 185 °C): 1% 4-(*m*-methoxyphenyl)butanal (6.8-min retention time), 25% **13** (25 min), 71% **12** (31 min), 1% chlorohydrin (40 min), and 2% diol. Internal-standard (*m*-methoxybenzyl alcohol) GC analysis showed that **12** and **13** are formed in combined yields of 30–34%. Each product was isolated by preparative GC (reinjection showed no rearrangement).

12: mp 52–54 °C (lit.[17] mp 52–54 °C); ^1H NMR ($CDCl_3$) δ 1.6–2.2 (m, 2 H), 1.8 (s, OH), 2.5–3.2 (m, 4 H), 3.7 (s, 3 H), 3.8–4.4 (m, CH–O), 6.6–7.3 (m, 3 H); IR (AgCl disks) 3200–3600 (OH), 1250 (CH_3O), 1040 (COH), 800 (1,2,4-trisubstituted benzene). The spectra and GC retention times were identical with those obtained from the $LiAlH_4$-reduction product of 6-methoxy-2-tetralone (Aldrich Chemical Co.).

13: mp 105–106 °C (lit.[40] mp 105.5–106.5 °C); ^1H NMR and IR data matched those reported[40] for the compound already synthesized by a different method.

Reinvestigation.[17] Treatment of 2.5 g of **8** with 6 g of trifluoroacetic acid (TFA) in 10 mL of CH_2Cl_2 with refluxing for 2 h and subsequent hydrolysis of the TFA esters with 6% methanolic HCl[17] (or KOH/ethanol) for 2 h gave 18–30% cyclization products (**12**:**13** = 23:77) and 70–82% 4-(*m*-methoxyphenyl)butane-1,2-diol. Treatment of **12** under the reaction conditions and subsequent hydrolysis did not yield observable amounts (~2%) of **13**. Since the $SnCl_4$-promoted reactions gave **12** and **13** directly, it seems doubtful that these products arise predominantly during ester hydrolysis (a possibility suggested earlier[17]).

1,2-Benzocyclohepten-3-ylmethanol (14)[20] and 2-(1,2,3,4-Tetrahydro-1-naphthyl)ethanol (15).[41] The FC procedure with **9** (in CH_2Cl_2) gave (retention time, FFAP column, 185 °C) 1% 6-phenylheptanal (4.2 min), 61% **14** (13.7 min), 18% **15** (15.1 min), 5% 3-chloro-6-phenylheptan-1-ol[42] (19.2 min), and 2-chloro-6-phenylheptan-1-ol (24.5 min) on the bases of IR, NMR, and GC–MS data. Samples of **14** and **15** provided by Rolf Huisgen[20,41] allowed unambiguous identification of these compounds.

14:[20] ^1H NMR (CCl_4) δ 1.2–2.0 (m, 6 H), 2.7–3.2 (m, 4 H), 3.6–4.0 (m, CH_2O), 7.0 (s, 4 Ar H); IR (AgCl disks) 3200–3600 (OH), 1020 (COH), 750 (ortho) cm^{-1}.

15:[41] ^1H NMR (CCl_4) δ 1.4–2.3 (m, 6 H), 2.5–3.2 (m, 3 H), 3.6 (t, 2 H, J = 7 Hz), 3.4 (s, OH), 6.9–7.1 (m, 4 Ar H); IR (AgCl disks) 3200–3600 (OH), 1040 (COH), 750 (ortho) cm^{-1}.

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Registry No. 1, 4436-24-2; 2, 51410-45-8; 3, 74769-16-7; *cis*-4, 36004-03-2; *trans*-4, 32215-84-2; 5, 1126-76-7; 6, 86088-36-0; *cis*-7, 86088-37-1; *trans*-7, 86088-38-2; 8, 1202-38-6; 9, 86088-39-3; 10, 66377-63-7; 11, 86088-40-6; 12, 1447-87-6; 13, 53568-06-2; 14, 86088-41-7; 15, 68480-12-6.

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(42) Tentative identification inferred from the presence of **15**. It is definitely a second chlorohydrin, however, as shown by GC–MS.