nuclear magnetic resonance, and mass spectrometry, in addition to gas chromatography.

Reaction of Benzyl Alcohol in the Absence of a Solvent. Benzyl sulfides were isolated as white needles in 77% yield when 5.4 g (50 mmol) of benzyl alcohol was treated with 0.34 g (1.0 mmol) of $Co_2(CO)_8$ following the general procedure except for the absence of a solvent.

General Procedure for the Carbonylation of Alcohols to Esters. The procedure used was identical with the previous one except for the use of an alcohol–water mixture instead of water–hexane, hexane, or hexane–ether.

Acknowledgment. We are indebted to British Petroleum and to the Natural Sciences and Engineering Research Council of Canada for support of this research.

Registry No. 1 (R = H), 100-51-6; 1 (R = 2-CH_3), 89-95-2; 1 (R = 3-CH_3), 587-03-1; 1 (R = 4-CH_3), 589-18-4; 1 (R = 4-C_2H_5), 768-59-2; 1 (R = 4-CH_3O), 105-13-5; 1 (R = 4-C_2H_5O), 6214-44-4; 1 (R = 3,4-CH_3O), 93-03-8; 1 (R = 2,4-CH_3O), 7314-44-5; 2 (R = H), 100-53-8; 2 (R = 2-CH_3), 7341-24-4; 2 (R = 3-CH_3), 25697-56-7; 2 (R = 4-CH_3), 4498-99-1; 2 (R = 4-C_2H_5), 4946-13-8; 2 (R = 4-CH_3O), 6258-60-2; 2 (R = 4-C_2H_5O), 76542-25-1; 2 (R = 2,4-CH_3O), 114719-65-2; 3 (R = H), 108-88-3; 3 (R = 2-CH_3), 95-47-6; 3 (R = 3-CH_3), 108-38-3; 3 (R = 4-CH_3), 106-42-3; 3 (R = 4-C_2H_5), 622-96-8; 3 (R = 4-CH_3O), 104-93-8; 3 (R = 4-C_2H_5O), 622-60-6; 3 (R = 3,4-CH_3O), 494-99-5; 3 (R = 2,4-CH_3O), 38064-90-3; 4 (R = H, R′ = C_2H_5), 101-97-3; 4 (R = 3-CH_3, R′ = C_2H_5), 40061-55-0; 4 (R = 4-CH_3, R′ = C_2H_5), 14062-19-2; 4 (R = 4-CH_3, R′ = CH_3), 23786-13-2; 4 (R = 4-C_2H_5, R′ = C_2H_5), 14062-20-5; 4 (R = 4-CH_3O, R′ = C_2H_5), 14062-18-1; 4 (R = 4-C_2H_5O, R′ = C_2H_5), 40784-88-1; 4 (R = 3,4-CH_3O, R′ = C_2H_5), 18066-68-7; 4 (R = 3,4-CH_3O, R′ = CH_3), 15964-79-1; 4 (R = 3,4-CH_3O, R′ = n-C_4H_9), 89723-27-3; 4 (R = 2,4-CH_3O, R′ = C_2H_5), 92741-81-6; $Co_2(CO)_8$, 10210-68-1; H_2S, 7783-06-4; $Co_4(CO)_{12}$, 17786-31-1; $Co(OAc)_2$, 71-48-7; $Co(acac)_2$, 14024-48-7; $Co_2(CO)_4(dmb)_2$, 33009-59-5; $[Rh(CO)_2Cl]_2$, 14523-22-9; $Rh_6(CO)_{16}$, 28407-51-4; dibenzyl sulfide, 538-74-9; bis(3-methylphenyl) disulfide, 20333-41-9; bis(4-methylphenyl) disulfide, 103-19-5; bis(4-ethylbenzyl) sulfide, 114719-63-0; bis(4-ethoxybenzyl) sulfide, 34106-64-4; 2-naphthalenemethanol, 1592-38-7; 2-naphthalenemethanethiol, 6258-60-2; 2-methylnaphthalene, 91-57-6; bis(4-methylbenzyl) sulfide, 13250-88-9; bis(4-ethoxybenzyl) sulfide, 33837-70-6; bis(3,4-dimethoxybenzyl) sulfide, 110055-34-0; bis(2,4-dimethoxybenzyl) sulfide, 114719-64-1.

Friedel–Crafts Cyclialkylations of Some Epoxides. 3.[1,2] Cyclizations of Tertiary and Meta-Substituted Arylalkyl Epoxides

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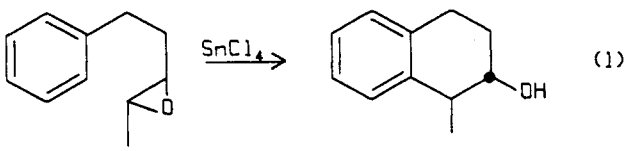
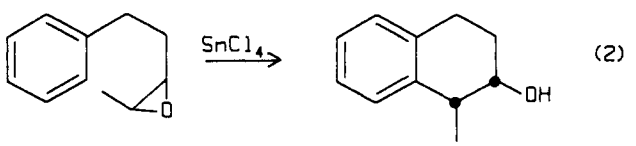
The intramolecular cyclization of aryl groups to tertiary epoxide positions was investigated, and the results were used to test the applicability of Baldwin's rules to this specific class of reactions. As a probe into the mechanism of reactions studied earlier, the cyclizations of some meta-substituted 1,2-epoxy-5-phenylpentanes were examined to determine positional selectivities. The data obtained were compared with those of other studies, and comments are made on the reaction mechanism.

Although epoxy–ene cyclizations have been extensively investigated,[3] epoxy–arene cyclizations (called cyclialkylations[4a]) have received only recent attention.[1,4] Yet despite their recent appearance, epoxy–arene cyclizations have already been useful in the synthesis of natural products.[4b,c,5] In our earlier studies,[1,4a] we determined the relative facility of cyclialkylation at primary and secondary epoxide positions to form five-, six-, and seven-member rings. We also demonstrated that several of the cyclizations are stereospecific (eq 1 and 2), catalytic, selective,



(1)



(2)

high-yield reactions. These processes involve minimal rearrangements, particularly when compared to the cyclialkylations of arylalkyl halides, alcohols, and alkenes.[6] In a linear free energy relationship study, we presented evidence that epoxide ring opening is important in determining the rate of the reaction[1] except where electron-withdrawing groups are attached to the aromatic ring.

We now complete these studies with this report on the relative facility of cyclialkylations at tertiary epoxide positions and on the positional selectivities of the cyclialkylation of meta-substituted arenes at secondary epoxides.

Results and Discussion

In earlier work, we were unable to cyclize tertiary arylalkyl epoxides.[2a] Similarly, in a report directed toward

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(1) Part 2: Taylor, S. K.; Davisson, M. E.; Hissom, B. R., Jr.; Brown, S. L.; Pristach, H. A.; Schramm, S. B.; Harvey, S. M. *J. Org. Chem.* **1987**, *52*, 425.

(2) (a) Presented in part at the 185th National Meeting of American Chemical Society, Seattle, WA, March 1983, and the (b) 193rd National Meeting of American Chemical Society, Denver, CO, April 1987.

(3) (a) van Tamelen, E. E. *Acc. Chem. Res.* **1975**, *8*, 152 and references therein. (b) van Tamelen, E. E., Loughhead, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 869. (c) Goldsmith, D. J. *Ibid.* **1962**, *84*, 3913. (d) Goldsmith, C. J. *J. Org. Chem.* **1965**, *30*, 2264. (e) Harding, K. E.; Cooper, J. L.; Puckett, P. M. *Ibid.* **1979**, *44*, 2834.

(4) (a) Taylor, S. K.; Hockerman, G. H.; Karrick, G. L.; Lyle, S. B.; Schramm, S. B. *J. Org. Chem.* **1983**, *48*, 2449. (b) Tanis, S. P.; Herrinton, P. M. *Ibid.* **1983**, *48*, 4572. (c) Tanis, S. P.; Raggon, J. W. *Ibid.* **1987**, *52*, 819.

(5) Burnell, R. H.; Dufour, J.-M. *Can. J. Chem.* **1987**, *65*, 21.

(6) (a) Khalaf, A. A.; Roberts, R. M. *J. Org. Chem.* **1972**, *37*, 4227; (b) *Ibid.* **1966**, *31*, 89; (c) *Ibid.* **1969**, *34*, 3571.

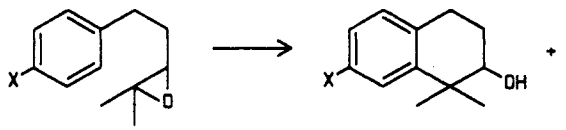
0022-3263/88/1953-3309$01.50/0

Table I. Tertiary Epoxide Cyclialkylation Products

epoxide	lewis acid (equiv)[a]	time, h	solvent	product distribution % 2	3	4	6	7	% GC yield of cyclization product
1a	$SnCl_4$ (0.1)	4	CH_2Cl_2	29	29	42			23
1a	$BF_3{\cdot}OEt_2$ (0.1)	4	CH_2Cl_2	28	64.5	7.5			24
1a	ZnI_2 (2)	4	CH_2Cl_2	25	65	3[b]			22
1b	$SnCl_4$ (0.1)	4	CH_2Cl_2	46	37	17			47
1b	$BF_3{\cdot}OEt_2$ (0.1)	4	CH_2Cl_2	40.5	50.5	9			42
1b	ZnI_2 (2)	4	CH_2Cl_2	41	54.5	4.5			37
5	$BF_3{\cdot}OEt_2$ (0.1)	4	CH_2Cl_2				60	38[c]	52
5	$BF_3{\cdot}OEt_2$ (0.1)	0.25	CH_2Cl_2				60	40	53
5	$BF_3{\cdot}OEt_2$ (0.1)	4	heptane				13	87	8
5	$SnCl_4$ (0.1)	4	heptane				8	88[d]	5

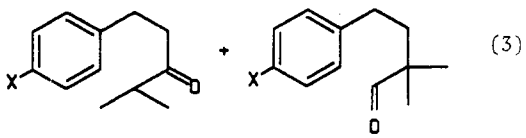
[a] Equivalents of Lewis acid relative to epoxide. [b] 7% unidentified compounds. [c] 2% unidentified compounds. [d] 4% unidentified compound.

oxidative cyclizations with mercury salts, Julia and Labia[7] unsuccessfully attempted to cyclize 2,3-epoxy-2-methyl-5-phenylpentane (**1a**, eq 3) and obtained only a 20% yield of cyclization product from 1,2-epoxy-2-methyl-5-phenylpentane (**5**, eq 4).[8] We now can report to have found conditions that successfully promote epoxide cyclialkylation at tertiary epoxide positions. Our results are in accord with those of Tanis[4b,c] and co-workers and the expectations of Baldwin's rules.[9,10]



1a, X=H
1b, X=MeO

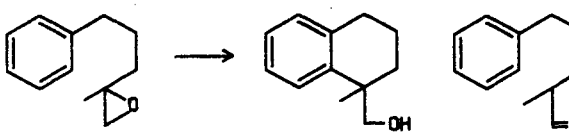
2a
2b



(3)

3a
3b

4a
4b



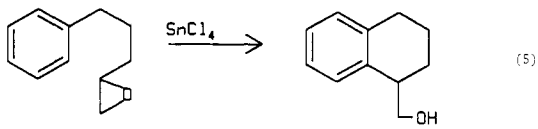
(4)

5 **6** **7**

When treated with typical Lewis acids, **1a** gives low but significant yields (Table I) of the cyclization product **2a** (eq 3) if dry CH_2Cl_2 is used as solvent. None of this product is obtained if heptane[2a] or benzene[7] are used as reaction solvents. Catalytic quantities of $SnCl_4$ and $BF_3{\cdot}OEt_2$ are sufficient to promote the reaction. The reactions must be run under very dilute conditions to minimize intermolecular reactions. Particularly noteworthy is the large quantity of **4a**, a skeletal rearrangement product, obtained when $SnCl_4$ is used as the Lewis acid. No other promoter gave nearly the quantity of this product as did $SnCl_4$ (Table I).

As would be expected, a methoxy aromatic group promotes the alkylation reaction. Treating **1b** with $SnCl_4$ produces **2b** in 47% VPC yield. Epoxides **1a** or **1b** (whose cyclizations would be classified as endo[9,4b,c]) give lower cyclization yields than **5**, which cyclizes through the generally preferred exo process. When heptane is used as a nonpolar reaction solvent for the reaction of **5**, the yield (Table I) is indeed reduced to approximately that observed by Julia and Labia.[7]

The fact that the exo epoxy–arene cyclization is more facile than the comparable endo process (even when the aryl group is highly activated) demonstrates the critical importance of the stereoelectronic requirements of the transition state. As a further example of the fact that Baldwin's rules can be applied to epoxy–arene cyclizations, the endo cyclization shown in eq 1 occurs in 67% yield whereas the preferred exo cyclization of eq 5 occurs in 91% yield.[4a]

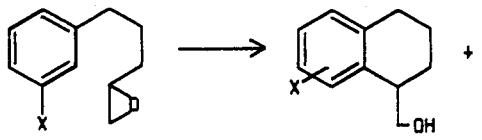


(5)

Earlier kinetic work on the ring closures of para-substituted 1,2-epoxy-5-phenylpentanes[1] established that the substrate selectivities are small ($k_{toluene}/k_{benzene}$ = 2.2:1[11]). The investigation of meta-substituted 1,2-epoxy-5-phenylpentanes (eq 6) affords us the opportunity to determine positional selectivities.

Table II shows that, except when substituted with strong electron-withdrawing groups (CF_3), meta-substituted 1,2-epoxy-5-arylpentanes give cyclization products in high yields.[12] For these compounds, $SnCl_4$ was the best promoter. The ratios of the ortho:para substitution products (the ratios of 8- to 6-substituted 1,2,3,4-tetrahydronaphthalenemethanols) reflect the positional selectivity of the cyclization process.[1] Since they are quite low (approximately 1:1.6) it seems doubtful that this reaction occurs via a π-complex mechanism.[12-15] The same low

(7) Julia, M.; Labia, R. *Bull. Soc. Chim. Fr.* **1972**, 4151.
(8) Julia (ref 7) did obtain a reasonable yield of cyclization product when a *m*-methoxy activating group was attached to the aromatic ring, but this is the only instance in which a respectable yield was obtained.
(9) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734.
(10) Baldwin did not discuss epoxide cyclization to aromatic groups, but Tanis' work and this report show that these principles are very useful in accounting for the relative facility of numerous epoxy–arene ring closures.
(11) Other workers observed similar results in intermolecular epoxide alkylations. See: Inoue, M.; Chano, K.; Itoh, O.; Sugita, T. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 458.
(12) Other products can occur if the reaction goes through an Ar_1-5 or spiro-type intermediate, see: Ando, T.; Yamawaki, J.; Saito, Y.; Takai, Y.; Yamataka, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2348. We already discussed this possibility in ref 4b. The products most likely to occur by this pathway are the 7-substituted 1,2,3,4-tetrahydronaphthalenemethanols, which were prepared earlier (ref 1). The relative amounts of these products are <1% (below detectable limits), 2.2%, 1%, and 1.8% for CH_3O, CH_3, Cl, and CF_3 groups, respectively, as shown by capillary GC (DB wax column).
(13) Stock, L. M.; Brown, H. C. *Adv. Phys. Org. Chem.* **1963**, *1*, 35.



8-X 6-X

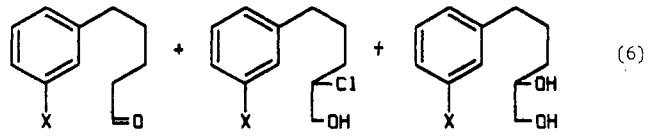
8 9 10

a, X=CH_3O

b, X=CH_3

c, X=Cl

d, X=CF_3



(6)

11 12 13

positional and substrate selectivities were obtained by other workers in the intermolecular Friedel–Crafts reactions of propylene oxide with various aromatics.[11]

A catalytic quantity of Lewis acid was generally sufficient to effect these reactions.[1] But in an attempt to demonstrate a general procedure that would complete the reaction of all epoxides, we treated the epoxides with 2 equiv of $SnCl_4$ and stirred the solutions overnight. The resulting alcohol products were surprisingly stable to these conditions with the exception of 6-methoxy-1,2,3,4-tetrahydro-1-naphthalenemethanol.[16]

Conclusions

Combined with results from our first two reports,[1,4a] this work demonstrates that the relative facility of epoxy–arene cyclization (with respect to the degree of epoxide substitution) is secondary > tertiary > primary. The relative ease of epoxide cyclialkylation with respect to the size of the ring being formed is 6 > 7 > 5.[17] These findings, may be used to predict the relative yield of these reactions and are consistent with Baldwin's rules. The generally high yields and selectivities[1,4,5] as well as the catalytic nature of many of these reactions make them useful synthetically, as has been shown by this and other recent reports.[4b,c,5] In a future report, we will discuss the relative facility of epoxide cyclization to double bond and aromatic positions.

Experimental Section

Equipment used was described earlier.[4a] Also, a Hewlett-Packard 5790B mass selective detector and a 5995A mass spectrometer equipped with capillary VPC were used for mass spectral measurements. A 30-m SPB-5 capillary column was used to determine product distributions and yields of the tertiary epoxide reactions, and a 30-m DB wax column was used to analyze the meta-substituted epoxide reaction products. Compounds **1a**, **3a**, **4a**, **5**, **6**, and **7** have been described elsewhere.[7] The olefinic precursors to epoxides **8a–d** were prepared from the reaction of the Grignard reagent of the appropriately substituted (2-chloroethyl)benzene and allyl bromide as described earlier.[4a] The olefinic precursor of **1b** was prepared analogously from benzylmagnesium chloride and 4-bromo-2-methyl-2-butene. The epoxides were all prepared by epoxidation of the olefins with MCPBA.[4a] Solvents used were dried by distillation from CaH_2 (under N_2) immediately before use. Cyclization yields of **8a–d** were determined by GC using 2-indanol as an internal standard. Cyclization yields of **1a,b** were determined similarly by using biphenyl as internal standard. Compounds **4b** and **11–13** were identified by GCMS. A freshly opened bottle of boron trifluoride etherate was used as received; $SnCl_4$ was dispensed from an Aldrich Sure/Seal bottle.

2,3-Epoxy-2-methyl-5-(*p*-methoxyphenyl)pentane (1b): bp 66–68 °C (0.03 mm); NMR (CCl_4) δ 1.1 (s, 3 H), 1.2 (s, 3 H), 1.5–1.9 (m, 2 H), 2.7 (m overlapping a t, 1 H), 2.4–2.7 (t, 3 H, J = 7 Hz), 3.7 (s, CH_3O), 6.4–7.1 (A_2B_2, 4 Ar H); IR (NaCl disks) 1520 (s), 1250 (s, ether), 1050 (m), and 840 (m, para) cm^{-1}; mass spectrum, exact m/e calcd for $C_{13}H_{18}O_2$ 206.131, found 206.136.

1,2-Epoxy-5-(*m*-methoxyphenyl)pentane (8a): bp 87–89 °C (0.1 mm); NMR (CCl_4) δ 1.1–2.0 (m, 4 H), 2.1–2.8 (m, 5 H), 3.6 (s, CH_3O), 6.3–7.2 (m, 4 Ar H); IR (AgCl disks) 1250 (s, ether), 850, 770, and 690 (m, meta) cm^{-1}; mass spectrum, exact m/e calcd for $C_{12}H_{16}O_2$ 192.1150, found 192.1135.

1,2-Epoxy-5-*m*-tolylpentane (8b): bp 83–84 °C (0.6 mm); NMR (CCl_4) δ 1.2–2.1 (m, 4 H), 2.3 (s, CH_3), 2.2–3.0 (m, 5 H), 6.8–7.2 (m, 4 Ar H); IR (AgCl disks) 1610 (m, aromatic) 850, 780, and 695 (s, meta) cm^{-1}. Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.85; H, 9.44.

1,2-Epoxy-5-(*m*-chlorophenyl)pentane (8c): bp 100–101 °C (0.6 mm); NMR (CCl_4) δ 1.2–2.2 (m, 4 H), 2.3–3.2 (m, 5 H), 7.3 (s, 4 Ar H); IR (AgCl disks) 1080 (s), 870, 780, and 690 (m, meta) cm^{-1}; mass spectrum, exact m/e calcd for $C_{11}H_{13}ClO$ 196.0654, found 196.0645.

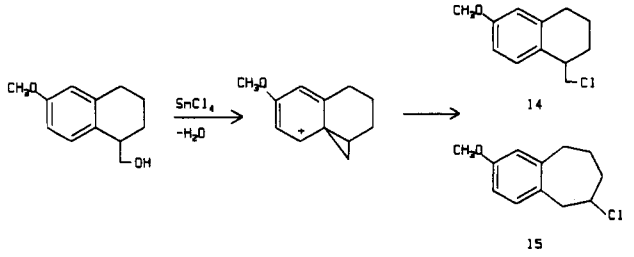
1,2-Epoxy-5-[*m*-(trifluoromethyl)phenyl]pentane (8d): bp 89–90 °C (1.2 mm); NMR (CCl_4) δ 1.2–2.2 (m, 4 H), 2.2–3.0 (m, 5 H), 7.3 (br s, 4 Ar H); IR (AgCl disks) 1320 (s, CF_3), 1170 (s, CF_3), 1120 (s, CF_3), 850, 800, and 700 (s, meta) cm^{-1}. Anal. Calcd for $C_{12}H_{13}F_3O$: C, 62.61; H, 5.69. Found: C, 62.26; H, 5.92.

General Procedure for Tertiary Epoxide Cyclization. The following procedure is representative. To a solution of 15 mL dry CH_2Cl_2 and Lewis acid (e.g., $BF_3{\cdot}OEt_2$, 12 μL, 0.1 mmol) was added dropwise (under N_2) a solution of **1b** (206 mg, 1 mmol) in 2 mL of dry CH_2Cl_2. The resulting solution was stirred at room temperature 4 h and then poured into a mixture of 50 mL of saturated aqueous NH_4Cl and 50 mL ether at 0 °C. The layers were separated, and the aqueous layer was extracted with ether. The combined organic layers were washed with 5% aqueous $NaHCO_3$ and saturated aqueous NaCl and dried ($MgSO_4$). After filtration and concentration on a rotary evaporator (no loss of products occurred during this procedure), the oil was combined with a known quantity of biphenyl and gas chromatographed (30-m SPB-5 capillary column) to determine both the product distribution and the GC yield of the cyclization product. The products were isolated by semipreparative HPLC using an 8 mm × 30 cm column packed with 10-μm silica gel. Product distributions are listed in Table I. A mobile phase of 2:88:10

(14) Olah, G. A. *Acc. Chem. Res.* **1971**, *4*, 240.

(15) An alternative interpretation exists: Ridd, J. H. *Acc. Chem. Res.* **1971**, *4*, 248.

(16) 6-Methoxy-1,2,3,4-tetrahydro-1-naphthalenemethanol rearranged to two halogen-containing compounds that could only be separated by capillary GC. On the basis of experiments (Huisgen, R.; Seidl, G. *Chem. Ber.* **1963**, *96*, 2740. Huisgen, R.; Seidl, G.; Wimmer, I. *Tetrahedron* **1964**, *20*, 623) on the solvolysis of the tosylate of 1,2,3,4-tetrahydro-1-naphthalenemethanol and spectral information on the actual product mixture, we have tentatively identified these two compounds as **14** and **15**, which arise by the pathway shown below. The 6-methoxy isomer would certainly be the most activated compound toward this type of demonstrated reaction.[17,18] When the compound was synthesized independently and subjected to our reaction conditions, it did rearrange to the same compounds.



(17) We were unable to form five-membered rings by epoxide cyclization. See Stork and Cohen (Stork, G.; Cohen, J. F. *J. Am. Chem. Soc.* **1974**, *96*, 5270) and ref 7 for explanations of this behavior. Boeckman et al. (Boeckman, R. K., Jr.; Bruza, K. J.; Heinrich, G. R. *J. Am. Chem. Soc.* **1978**, *100*, 7101) report five-membered ring formation via an epoxide cyclization.

Table II. Meta-Substituted Epoxide Cyclialkylation

epoxide[a]	9/10[b]	product distribution, % 9	10	11	12	13	9 + 10, GC yield, %
8a[c]	0.64	38	59	3			95
8b	0.64	34	53	9	1	3	86
8c	0.78	38	49	4	4	5	86
8d		60[d-f]		3	26	5	50

[a] Each epoxide was treated with 2 equiv of $SnCl_4$ for 19 h. [b] Indicates the relative amount of ortho to para cyclization product, or 8-methoxy- to 6-methoxy-1,2,3,4-tetrahydro-1-naphthalenemethanol ratio. [c] Reaction time shortened to 1 h. [d] Reaction mixture was refluxed 4 h and stirred 44 h. [e] 6% unreacted epoxide remained. [f] Only one product could be detected by GC. This compound was identified as the 6-substituted compound.

CH_3CH_2OH/hexane/CH_2Cl_2 was used to isolate the two products **2b** and **3b** (32- and 16-mL retention volumes, respectively).

7-Methoxy-1,1-dimethyl-1,2,3,4-tetrahydro-2-naphthol (2b): mp 85–88 °C (lit.[18] 91–93 °C); spectral data matched those of an independently prepared sample.[18]

5-(*p*-Methoxyphenyl)-2-methyl-3-pentanone (3b): NMR (CCl_4) δ 1.0 (d, 6 H), 2.3–2.7 (m, 1 H), 2.5–2.8 (m, 4 overlapping H), 3.7 (3, OCH_3), 6.5–7.2 (A_2B_2, 4 Ar H, J = 9 Hz); IR (NaCl disks) 1710 (s, C=O), 1250 (s, OCH_3), and 830 (s, para) cm^{-1}: mass spectrum, exact m/e calcd for $C_{13}H_{18}O_2$ 206.1307, found 206.1358.

1,1-Dimethyl-1,2,3,4-tetrahydro-2-naphthol[18] (2a) was prepared and isolated by the above procedures: NMR (CCl_4) δ 1.2 (s, 3 H), 1.3 (s, 3 H), 1.7–2.1 (m, 3 H), 2.6–3.0 (t, 2 H, J = 7 Hz), 3.5–3.7 (m, 1 H), 6.9–7.3 (m, 4 H); IR (NaCl disks) 3200–3700 (br, OH), 1040 (s, alcohol), and 770 (s, ortho) cm^{-1}: mass spectrum, exact m/e calcd for $C_{12}H_{16}O$ 176.1201, found 176.1214.

General Friedel–Crafts Cyclization Procedure for Meta-Substituted Epoxides. To a solution of 12 mmol of $SnCl_4$ in 80 mL of dry CH_2Cl_2 was added dropwise (over 10 min) 6 mmol of **8** in 8 mL of CH_2Cl_2. The solution was then stirred 19 h (for **8a** and **8d**, stirring times were 1 and 48 h, respectively). The reaction solution was then added to ice/water, and 80 mL of ether was added to the mixture. The organic layer was washed with 5% aqueous $NaHCO_3$ (three times) and 15% aqueous NaCl, dried ($MgSO_4$), and evaporated. When **8a** was allowed to react 18 h, the product distribution was 31% of a mixture of chloride-containing compounds,[16] 38% ortho alkylation product (8-methoxy-1,2,3,4-tetrahydro-1-naphthalenemethanol), and 31% 6-methoxy isomer. When the reaction time was reduced to 1 h, the chloro compounds were present at <1% and the relative quantity of the 6-isomer increased (see Table II). The chloro compounds showed an exact mass of 212.0782 (calcd 212.0790 for $C_{12}H_{15}{}^{37}ClO$), 210.0808 (calcd 210.0811 for $C_{12}H_{15}{}^{35}ClO$), and 161.0979 ($M^+ - CH_2Cl$, base peak).

8-Methoxy-1,2,3,4-tetrahydro-1-naphthalenemethanol (9a): mp 70–72 °C; NMR (CCl_4) δ 1.3 (s, OH), 1.5–2.3 (m, 4 H), 2.5–2.9 (t, 2 H, J = 7 Hz), 3.0–3.3 (m, 1 H), 3.4–3.6 (m, 2 H), 3.8 (s, CH_3O), 6.4–7.1 (m, 3 H); IR (AgCl disks) 3200–3600 (OH), 1250 (CH_3O), 1030 (m, hydroxyl), 765, and 730 (1,2,3-trisubstituted aromatic) cm^{-1}; mass spectrum, exact m/e calcd for $C_{12}H_{16}O_2$ 192.1150, found 192.1156.

6-Methoxy-1,2,3,4-tetrahydro-1-naphthalenemethanol[19] (10a): bp 111–112 °C (0.05 mm); 3,5-DNB, mp 145.5–147.5 °C; NMR (CCl_4) δ 1.5–2.2 (m, 4 H), 2.5–3.1 (m, 4 H including OH), 3.6 (d, 2 H, J = 7 Hz), 3.65 (s, OCH_3), 6.4–7.1 (m, 3 Ar H); IR (AgCl disks) 3200–3700 (br, OH), 1240 (s, OCH_3), 1040 (s, hydroxyl), 845, and 805 (s, 1,2,4-trisubstituted aromatic) cm^{-1}: mass spectrum, exact m/e calcd for $C_{12}H_{16}O_2$ 192.1150, found 192.1165.

6- and 8-Methyl-1,2,3,4-tetrahydro-1-naphthalenemethanols (9b and 10b) were obtained as a mixture from the cyclization procedure, bp 90–92 °C (0.1 mm). GC, NMR, and IR indicated a mixture of the two isomers [6 ft × $^1/_8$ in. 10% DEGS column, 180 °C, overlapping peaks at 36 (6-methyl) and 39.5 min (8-methyl isomer)]; NMR overlapping $ArCH_3$ peaks at δ 2.34 and 2.28; IR 760 (1,2,3-trisubstituted aromatic) and 810 (1,2,4-trisubstituted aromatic); mass spectra (m/e), of both compounds were very similar: 176 (M^+, 18), 145 ($M^+ - CH_2OH$, 100). We were unable to separate the compounds by preparative GC or HPLC. However, attempted collection of the GC peak at 36 min gave a mixture that was enriched in the 6-methyl isomer as indicated by IR spectroscopy.

6- and 8-Chloro-1,2,3,4-tetrahydro-1-naphthalenemethanols (9c and 10c) were obtained from the cyclization as a mixture, bp 128–131 °C (0.8 mm), and the distillate was partially separated by preparative GC[20] (6 ft × 0.25 in. 10% OV17 column, 170 °C (0.8 mm); 6- and 8-isomers, 10- and 13.5-min retention times, respectively). GC peak 1 gave a strong IR band at 770 cm^{-1}, indicating it was the 8-chloro (1,2,3 trisubstituted) isomer. The unpurified product mixture gave IR bands at 810 and 870 cm^{-1}, which indicated the 6-chloro isomer **10c**. NMR (CCl_4) δ 1.2–2.3 (m, 5 H), 2.5–3.2 (m, 3 H), 3.5–4 (m, 2 H), 6.9–7.5 (m, 3 Ar H); mass spectra, m/e (relative intensity), of the two isomers were very similar: 198 (6), 196 (17), 165 (100), 129 (35), and 130 (40).

6-(Trifluoromethyl)-1,2,3,4-tetrahydro-1-naphthalenemethanol (10d). Only one of the isomers was detected by packed and capillary column GC: bp 120–121 °C (1.5 mm); NMR (CCl_4) δ 1.6–2.2 (m, 4 H), 2.6–3.1 (m, 4 H), 3.7 (d, 2 H, J = 7 Hz), 7.3 (s, 3 Ar H);[21] IR (AgCl disks) 3200–3600 (br, OH) 1315 (CF_3), 1120 (s), 1160 (s), 830, and 870 (1,2,4-trisubstituted aromatic) cm^{-1}; mass spectrum, m/e (relative intensity) 230 (M^+, 3) 212 ($M^+ - H_2O$, 23), 200 (22), 199 (100), and 159 (20). The other major product, **12**, showed mass spectral peaks, m/e (relative intensity), at 266 (1), 248 (10), 172 (100), 159 (75), 143 (25), and 109 (28).

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Registry No. **1a**, 40463-08-9; **1b**, 114423-21-1; **2a**, 1865-95-8; **2b**, 1865-78-7; **3a**, 40463-09-0; **3b**, 100765-45-5; **4a**, 40654-84-0; **4b**, 114423-22-2; **5**, 40463-17-0; **6**, 25634-94-0; **7**, 36613-11-3; **8a**, 114423-16-4; **8b**, 114423-23-3; **8c**, 114423-24-4; **8d**, 114423-25-5; **9a**, 114423-17-5; **9b**, 36052-28-5; **9c**, 114423-26-6; **10a**, 114423-18-6; **10b**, 106336-34-9; **10c**, 114423-27-7; **10d**, 114423-28-8; **11a**, 111171-92-7; **11b**, 102683-34-1; **11c**, 114423-31-3; **11d**, 114423-32-4; **12b**, 114423-19-7; **12c**, 114423-33-5; **12d**, 114423-34-6; **13b**, 114423-20-0; **13c**, 114423-35-7; **13d**, 114423-36-8; benzylmagnesium chloride, 6921-34-2; 4-bromo-2-methyl-2-butene, 870-63-3; 2-methyl-5-(*p*-methoxyphenyl)pent-2-ene, 4586-91-8; 5-(*m*-methoxyphenyl)pentene, 40463-20-5; 5-(*m*-chlorophenyl)pentene, 114423-29-9; 5-[*m*-(trifluoromethyl)phenyl]pentene, 114423-30-2; 5-(*m*-tolyl)pentene, 51125-15-6.

(18) Hill, J. A.; Johnson, A. W.; King, T. J.; Natori, S.; Tam, S. W. *J. Chem. Soc.* **1965**, 361.

(19) This compound was also made independently by treating 6-methoxy-2-tetralone with the Wittig reagent of methyltriphenylphosphonium bromide and then performing a hydroboration–oxidation on the product. The spectral data of this compound were identical with those of the compound isolated from epoxide cyclization. Treatment of this compound with $SnCl_4$ (under the cyclization conditions) resulted in a mixture that was 40% chloro rearrangement products.

(20) The peaks were cleanly separated, but during GC collection they "bled" into one another and were not isolated pure.

(21) Even 360-MHz NMR gave only a broad aromatic singlet and did not resolve the aromatic resonance peak into multiplets. Thus we could not characterize the aromatic substitution pattern by NMR.