Friedel–Crafts Cyclialkylations of Some Epoxides. 2.[1,2] Stereospecificity, Substituent, Product, and Kinetic Studies

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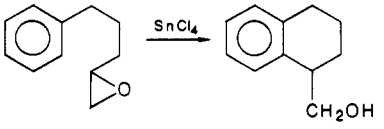
The relative facility of the cyclialkylation of several arylalkyl epoxides was investigated. Stereochemical studies on the cyclialkylation of *cis*- and *trans*-2,3-epoxy-5-phenylpentane establish that the stereospecificity of ring formation is as high as 97%. As expected, in substituent effect studies compounds with aromatic activating groups are shown to give higher yields than unsubstituted or deactivated analogues. However, a linear free energy relationship (LFER) study on aryl-substituted compounds (**5a–f**) suggests that electron-donating groups have surprisingly little influence on reaction rates. The optimized Friedel–Crafts procedure used herein markedly increases the yield of an intermolecular epoxide Friedel–Crafts reaction done earlier.

The cyclization of epoxides is of general interest to the field of bioorganic chemistry, particularly since these types of reactions are involved in the biosynthesis of many compounds, including cholesterol.[3-6] Although numerous reports exist on the biomimetic epoxy–olefin cyclizations,[3-8] little has been done on the cyclization (called "cyclialkylation", eq 1) of arylalkyl epoxides.[1,7] Our recent



(1)

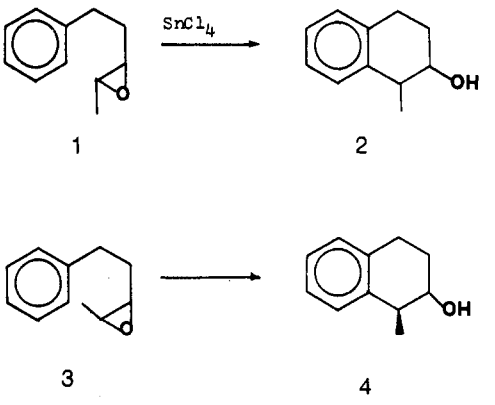
report[1] established the relative facility of the cyclialkylation of epoxides at primary and secondary positions to form five-, six-, and seven-membered rings. Other things being equal, the ease of cyclization with respect to ring size followed the order 6 > 7 > 5, whereas with the cyclialkylation of other functional groups (arylalkyl chlorides and alcohols) the order was 6 > 5 > 7.[8-10] Ring closure at secondary positions was more facile than at primary positions as is normally the case,[8-11] but with epoxides the difference was more pronounced. Since our report, other workers have demonstrated the utility of epoxy–arene cyclizations in the synthesis of natural products.[7b] We now report on the stereospecificity and kinetics of epoxide cyclialkylations.

Results and Discussion

Stereospecificity. To determine the stereospecificity of ring closure, we prepared *trans*- and *cis*-2,3-epoxy-5-phenylpentane (**1** and **3**, Scheme I) from the corresponding trans and cis olefins[12] by standard peracid epoxidation.[1] Treatment of a 93:7 mixture of **1**[13] and **3** with 2 equiv of $SnCl_4$ in CH_2Cl_2 by the method described earlier[1] gives the isomeric 1-methyl-1,2,3,4-tetrahydro-2-naphthols **2** and **4** (66% yield) in a trans:cis ratio of 94:6 (±2%) via an inversion mechanism. An intermolecular Friedel–Crafts study with optically active propylene oxide also showed remarkably high stereospecificity.[14]

A 4:96 mixture of **1** and **3** cyclized similarly in 63% yield to give a 13:87[15] ratio of **2**:**4**, corresponding to somewhat lower stereospecificity. Still, the demonstrated selectivity stands in marked contrast to the typical expectations of Friedel–Crafts reactions[9-11,16] (the side products for both cyclizations are essentially the same as that reported earlier for a mixture of **1** and **3**[1]) and suggests that a near-concerted reaction occurs.

Scheme I



Analysis of the isomeric ratios was done by GC and 360-MHz ^1H NMR. In a 360-MHz NMR spectrum, the methyl doublets of the isomers were sufficiently separated for integration of the reaction of **3** and the GC results agreed with the ratio determined. In the reaction of **1**, the quantity of product **4** was so small that NMR integration was not accurate and the isomeric ratio was determined by GC alone.

The hydroxy methine proton (HO-C-*H*) multiplet of **4**,

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(1) Part 1: Taylor, S. K.; Hockerman, G. H.; Karrick, G. L.; Lyle, S. B.; Schramm, S. B. *J. Org. Chem.* **1983**, *48*, 2449.
(2) Presented in part at the 185th American Chemical Society National Meeting, Seattle, WA, March 1983.
(3) (a) van Tamelen, E. E. *Acc. Chem. Res.* **1975**, *8*, 152 and references therein. (b) Johnson, W. S. *Bioorg. Chem.* **1976**, *5*, 51.
(4) (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.
(5) (a) Goldsmith, D. J. *J. Am. Chem. Soc.* **1962**, *84*, 3913. (b) Goldsmith, D. J.; Cheer, C. J. *J. Org. Chem.* **1965** *30*, 2264.
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(7) (a) Davidson, A. J.; Norman, R. O. C. *J. Chem. Soc.* **1964**, 5404. (b) Tanis, S. P.; Herrinton, P. M. *J. Org. Chem.* **1983**, *48*, 4572.
(8) (a) Khalaf, A. A.; Roberts, R. M. *J. Org. Chem.* **1972**, *37*, 4227; (b) **1966**, *31*, 89.
(9) Khalaf, A. A.; Roberts, R. M. *J. Org. Chem.* **1969**, *34*, 3571.
(10) Khalaf, A. A. *Indian J. Chem.* **1974**, *12*, 476.
(11) Khalaf, A. A.; Roberts, R. M. *J. Org. Chem.* **1971**, *36*, 1040.
(12) Benkeser, R. A.; Tincher, C. A. *J. Org. Chem.* **1968**, *33*, 2727.
(13) We reported this reaction earlier without regard to reaction stereochemistry (ref 1). Since then we developed capillary GC and high resolution NMR techniques to determine the ratio of geometric isomers.
(14) Nakajima, T.; Suga, S.; Sugita, T.; Ichikawa, K. *Tetrahedron* **1969**, *25*, 1807.
(15) Based on a 1:3 ratio of 4:96 for the starting epoxide.
(16) Olah, G. A. *Friedel–Crafts Chemistry*; Wiley-Interscience: New York, 1973; pp 59–62, 185–186.

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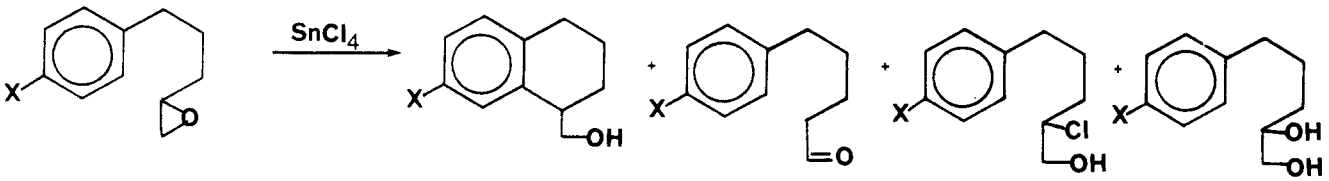
Scheme II



5a, X = CH_3O 6a 7a 8a 9a
5b, X = CH_3 6b 7b 8b 9b
5c, X = H 6c 7c 8c 9c
5d, X = F 6d 7d 8d 9d
5e, X = Cl 6e 7e 8e 9e
5f, X = CF_3 6f 7f 8f 9f

Table I. Epoxide Cyclialkylation Products

epoxide 5, X =	product distribution, % 6[a]	7	8	9
p-CH_3O	96	2	2	<1
p-CH_3	95	4	1	<1
m-CH_3	87[b]	9	1	3
H	91	7	1	1
p-F	89	0	2	9
p-Cl	87	3	3	7
p-CF_3[c]	84	3	3	10

[a] Within experimental error, the yield of the cyclization product is the same as the number in this column. [b] Ortho and para alkylation occurred in a 2:3 ratio, respectively. [c] Reaction time for this compound was 2 days longer than that of the other entries.

with an axial–equatorial methyl and hydroxyl substitution pattern, gives a doublet of triplets with apparent coupling constants of 7, 5, and 5 Hz. This agrees with predictions based on models which show similar dihedral angles for the protons involved. The hydroxy methine multiplet of **2** is an eight-line pattern which can be rationalized by coupling constants of 7, 6, and 3 Hz. The small coupling constant is consistent with a proton–proton dihedral angle predicted by models to be approximately 80° (assuming the methyl and hydroxyl substituents are predominantly in the equatorial–equatorial conformation).

Substituent Effects. Some reports suggest that cyclialkylation[1,7] and other epoxide Friedel–Crafts reaction[17-19] yields are dramatically influenced by aromatic substituents. We prepared a series of substituted epoxides (**5a–f**) (Scheme II) and investigated substituent effects and the efficiency of our optimized reaction procedure.[1] The good to excellent cyclialkylation yields (Table I; within experimental error, the GC yields of **6a–f** are the same as that shown in the second column) and the reaction selectivity demonstrate the usefulness of this ring-forming technique for a variety of substituted compounds. The yields are highest where the aromatic ring is activated, as would be expected. However, yields are even very good where the ring is deactivated by moderate electron-withdrawing groups.[20]

Table II. Cyclization Rate Constants and Linear Free Energy Parameters

X	$10^{-3}k'$[a]	σ	log (k_X/k_H)
p-CH_3O	2.69	−0.78[b]	0.74
p-CH_3	1.09	−0.31[b]	0.35
m-CH_3	0.625	−0.10[c]	0.17
H	0.49	0.0[b]	0.0
p-F	0.045	0.35[c]	−1.04
p-Cl	0.008	0.40[c]	−1.79

[a] The average of at least two kinetic runs. [b] σ_p^+ values taken from: Johnson, C. D. *The Hammett Equation*; Cambridge University Press: New York, 1973. [c] σ_m^+ values. These values are not as reliable as the others as explained in the text. Therefore the choice of σ values used is somewhat arbitrary, although σ_p^+ values do not correlate (σ_p^+ values predict *p*-F to be slightly activating, which is definitely not the case here).

Generally, these cyclizations are not accompanied by rearrangements.[1] Hence an excess of Lewis acid promoter (2 equiv of $SnCl_4$) has been used in a general procedure to ensure that reactions go to completion, even with a wide variety of epoxides. However, with air-sensitive material handling techniques, we can get excellent yields with catalytic quantities of $SnCl_4$. For example, **5c** cyclizes to **6c** in >90% GC yield in CH_2Cl_2 using a 35:1 molar ratio of epoxide:$SnCl_4$. However, the reactions described in Table I all involved 2 equiv of $SnCl_4$, very dilute conditions (to minimize intermolecular reactions), and overnight reaction times.[1] Also, the least reactive compound (**5f**) was stirred an extra 2 days to allow sufficient time for the reaction to go for completion. After carefully following the reactions (see kinetic work below), we found that these conditions allowed more than ample time for reactions to go to completion.

We felt that it would be instructive to investigate the reaction mechanism by kinetics, particularly since other work has been almost exclusively product studies.[3-5] Therefore we determined pseudo-first-order rate constants for cyclizations of epoxides **5a–e**, in a linear free energy (LFER) study.

To obtain reaction times that could be conveniently followed for the faster reacting compounds (e.g., **5a**), the kinetic runs were done at −5 °C using only 0.05 equiv of $SnCl_4$ relative to epoxide. The appearance of product[21]

(17) Taylor, S. K.; Lilley, G. L.; Lilley, K. J.; McCoy, P. A. *J. Org. Chem.* **1981**, *46*, 2709.
(18) Taylor, S. K.; Clark, D. L.; Heinz, K. L.; Schramm, S. B.; Westermann, C. D.; Barnell, K. K. *J. Org. Chem.* **1983**, *48*, 592.
(19) Inoue, M.; Sugita, T.; Ichikawa, K. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 174.
(20) We also investigated the nitro-substituted compound but could find no evidence for cyclialkylation with this compound. The presence of 5–10% impurities in the starting epoxide prevented us from obtaining analytical data. However, the lack of alkylation on nitrated aromatics is consistent with Friedel–Crafts alkylation behavior (see ref 16).

(21) The reactions of **5a–c** (and for X = *m*-CH_3) were followed to >90% completion. Cyclizations of **5d–f** could not be followed to >90% completion as the low temperature and aliquoting technique tended to slow down the reaction after about 24 h—well before the reactions **5d–f** were half complete. This was probably due to the introduction of water into the system. The same observations have been made by Franklin P. DeHaan (private communication).

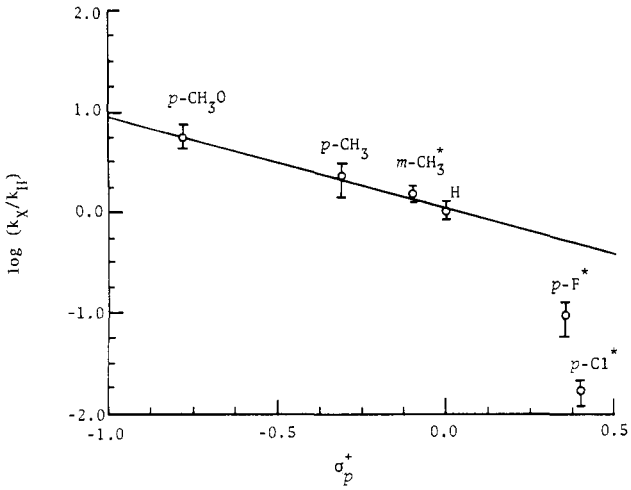
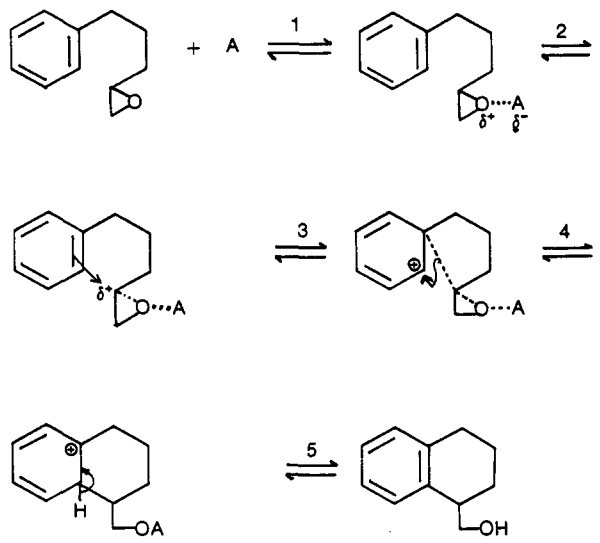


Figure 1. Linear free energy plot using σ_p^+ substituent constants and pseudo-first-order rate constants. Substituents with an asterisk were correlated using σ_m^+ constants.

Scheme III

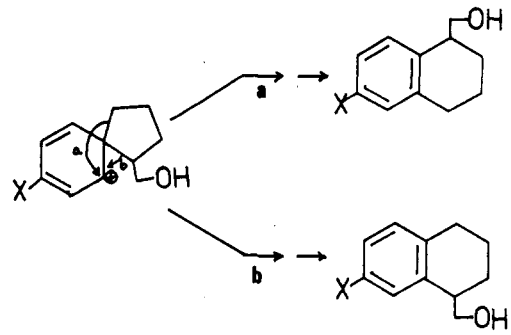


was followed for three reasons: (1) the disappearance of epoxide was difficult to follow since quenching the reaction inevitably leads to epoxide hydrolysis products; (2) following the cyclization product gives us information about that specific process; and (3) the greatest relative change in the initial reaction occurs in product and not reactant concentration.

The reactions were performed under nitrogen in dry CH_2Cl_2. Aliquots of the same $SnCl_4/CH_2Cl_2$ solution were used in each series of epoxide kinetic runs to ensure good comparative data. The reactions were followed by GLC after quenching each aliquot in saturated aqueous NaCl. The results of the kinetic runs correlated extremely well with σ_p^+ values (Figure 1) for the first four entries in Table II (σ_m values did not show any correlation). A modest ρ value of −0.91 for these substituents (*p*-CH_3O, *p*-CH_3, *m*-CH_3, and H) and the relatively similar rates of activated and unactivated aryl compounds suggests that aromatic participation is not highly significant in determining the reaction rate.[22]

In Scheme III, we outline the maximum possible number of mechanistic steps that can be inferred from numerous

Scheme IV



epoxide and cyclization studies.[23-27] The energies of activation of steps 1, 4, and 5 are known to be relatively low[23-27] and hence processes 2 and 3 appear to be the viable candidates for the rate-determining step. If 4 was rate-determining, aromatic substituent effects would be significant: again, they are not. Therefore we conclude that the rate-determining step is epoxide ring opening (step 2).

Although the data for electron-withdrawing substituents are less conclusive[20] than that for compounds bearing methoxy, methyl, and hydrogen groups, the apparent break in the slope of the LFER plot seems to suggest that a mechanistic change of some kind occurs for Cl- and F-substituted compounds. For these compounds the minimum ρ value is −4.5 (a typical value for electrophilic aromatic substitution is −4.5 to −12 if the electrophile is not fully charged[27,28]). We believe the best explanation for the mechanistic change is that the deactivating groups slow arenium ion formation to the point that it becomes rate-determining. Analogous mechanistic situations have been cited.[28-31]

Two modes of cyclization are possible. Direct attack of the electrophilic atom at the position meta to the substituent can occur. This mechanism is called Ar_2-6.[25] Alternatively, attack at the ipso position could give a spiro intermediate (Ar_1-5) that rearranges to the Ar_2-6 species[26] (see Scheme III), from which product is formed.

Mechanistic probes for distinguishing these two pathways have included double labeling experiments[26] which detect the rearrangement that can occur only via the Ar_1-5 pathway. In these reactions, the "double label" is built into the molecule already and therefore we determined the amount of rearrangement product (pathway a, Scheme IV) to determine the relative importance of this route.

(22) Another way of viewing this is to compare this case to intermolecular reactions where the reaction is zero order with respect to aromatic substrate (see Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, part A; Plenum: New York, 1977; p 388.

(23) Parker, R. E.; Isaacs, N. S. *Chem. Rev.* **1959**, *59*, 737.
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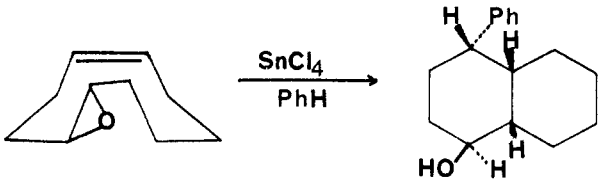
(25) Heck, R,; Winstein, S. *J. Am. Chem. Soc.* **1957**, *79*, 3114.
(26) (a) Jackman, L. M.; Haddon, V. R. *J. Am. Chem. Soc.* **1974**, *96*, 5130. (b) Gates, M.; Frank, D. L.; von Felten, W. C. *J. Am. Chem. Soc.* **1974**, *96*, 5138. (c) Ando, T.; Yamawaki, J.; Saito, Y.; Takai, Y,; Yamataka, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2348.
(27) (a) Schadt, F. L., III; Lancelot, C. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1978**, *100*, 228. (b) Stang, P. J.; Dueber, T. E. *J. Am. Chem. Soc.* **1977**, *99*, 2602.
(28) Brown, H. C.; Okamota, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979.
(29) Bartlett, P. A.; Brauman, J. I.; Johnson, W. S.; Volkmann, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 7502.
(30) Lambert, J. B. *Physical Organic Chemistry Through Solved Problems*; Holden-Day: San Francisco, 1978; pp 176–179.
(31) Other possibilities could account for the mechanistic change: (1) Compounds **5d** and **5e** could react via a species that is significantly carbocation-like (this does not exclude our proposed reason for the kinetic change). (2) The change could occur as the rate-determining step switches from π-complex formation to σ-complex formation, but the theory that π-complexes can be rate-determining has not been widely accepted (see ref *39* and references therein. Olah, G. A. *Acc. Chem. Res.* **1971**, *4*, 240. Ridd, J. H. *Ibid.* **1971**, *4*, 248). (3) The rate-determining step could switch from Ar_1-5 to Ar_2-6 but these changes do not cause the large rate differences observed for the deactivated aromatics (see ref 24 and 25).

Scheme V



As expected from our prediction of an unsymmetrical reactive species (the structure drawn between steps 3 and 4 of Scheme III), not much of the rearrangement pathway is observed. However, the trend is interesting. The relative amounts of these products[32] are 1.6, 3.2, 6, 8, and 0.4% for *p*-CH_3O, *p*-CH_3, *p*-Cl, *p*-F, and *p*-CF_3, respectively. The *p*-CF_3 group is the only meta director, and the small quantity is readily accounted for by assuming that the reaction occurs almost completely via the Ar_2-6 mechanism, i.e., direct meta attack.

The trend for the other groups argues against the possibility that the break in the LFER plot is due to an increase in relative quantity of mechanism occurring via the Ar_1-5 pathway (also, the relative rates of these two processes are fairly similar,[24,25] and such a change would not produce a large break in the LFER plot).

The data at first glance might indeed lead one to predict that more of the reaction occurs via the spiro intermediate (Scheme IV) as the groups go from activating to deactivating. But that is contrary to the expectations of directing effects and the direct observations of other investigations.[27] The data are consistent, however, with an increase in the symmetrical character of the reactive species where electron-withdrawing groups are involved. The greater ρ for these groups is consistent with that same expectation.

Earlier, we reported difficulty[33] in promoting intermolecular Friedel–Crafts reactions on a medium-ring epoxide with unactivated aromatics. With the new conditions reported herein, we have dramatically increased the yield of that same reaction from less than 2% to 70% isolated yield (Scheme V).

Experimental Section

Equipment used was described earlier.[1] Also, a Hewlett-Packard 5890A capillary GC and 5790B mass selective detector were used for some mass spectral measurements. The epoxides were synthesized from the appropriate arylalkenes[1] by treatment with in MCPBA as described earlier.[1] In product studies, the epoxides were cyclized by adding an epoxide/CH_2Cl_2 solution (6 mmol/8 mL) to 12 mmol of $SnCl_4$ in 80 mL of dry CH_2Cl_2, refluxing 4 h, stirring 19 h, and working up the solution as described before[1] (the CH_2Cl_2 freshly distilled from P_2O_5). GC yields were determined with 2-indanol as an internal standard. In kinetic studies, CH_2Cl_2 was distilled under N_2 from CaH_2 immediately before use and all reactions were done under dry N_2. The synthesis of *cis*- and *trans*-5-phenyl-2-pentene was accomplished as described by other workers[12] except that the cis isomer was prepared by reduction of the corresponding alkyne with Lindlar catalyst (rather than Raney nickel). Compounds **7**, **8**, and **9a–f** were identified by GCMS in all cases and NMR and IR in most cases.

***trans*-2,3-Epoxy-5-phenylpentane (1).** The compound was prepared by epoxidation[1] of the alkene:[12] bp 82–83 °C (2.2 mm); n^{25}_D 1.5044 (cis:trans = 7:93); 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 ArH); IR (AgCl disks) 860, 740, and 690 (monosubstituted benzene) cm^{-1}; mass spectrum, exact mass m/e calcd for $C_{11}H_{14}O$ 162.1045, found 162.1025.

***cis*-2,3-Epoxy-5-phenylpentane (3):** bp 88–89 °C (2.3 mm); n^{26}_D 1.5070 (cis:trans = 96:4); NMR (CCl_4) δ 1.1 (d, 3 H, J = 5 Hz), 1.7 (m, 2 H), 2.6 (m, 4 H), 7.1 (s, 5 ArH); IR (AgCl disks) 860, 745, 695 (s, monosubstituted benzene), and 1260 (m) cm^{-1}. Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.28; H, 8.57.

***trans*-1-Methyl-1,2,3,4-tetrahydro-2-naphthol[1] (2).** Cyclization of 1 in CH_2Cl_2 by a previously described method[1] gave 2 in 66% GC yield: bp 105–107 °C (0.2 mm); n^{20}_D 1.5457; 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, C*H*–O), 7.0 (m, 4 ArH); IR (AgCl disks) 3200–3600 (OH), 1030 (OH), and 755 (ortho) cm^{-1}.

***cis*-1-Methyl-1,2,3,4-tetrahydro-2-naphthol (4).** Cyclization by the above method was accomplished in 63% GC yield: bp 73–74 °C (0.05 mm); n^{25}_D 1.5484; NMR (CCl_4) δ 1.1 (d, 3 H, J = 7 Hz), 1.5–2.1 (m, 2 H), 2.6–3.2 (m, 4 H), 3.9 (m, 1 C*H*–O), 7.0 (m, 5 ArH); IR (AgCl disks) 3200–3600 (s, OH) and 755 (ortho) cm^{-1}: mass spectrum, exact mass m/e calcd for $C_{11}H_{14}O$ 162.1045, found 162.1042.

1,2-Epoxy-5-(*p*-methoxyphenyl)pentane (5a): bp 90–91 °C (0.05 mm); n^{29}_D 1.5169; NMR (CCl_4) δ 1.1–1.9 (m, 4 H), 2.1–2.3 (m, 1 H), 2.3–2.9 (m,, 4 H), 3.6 (s, CH_3O), 6.6–7.2 (A_2B_2, 4 ArH); IR (AgCl disks) 1240 (s, methoxy), 1015 (s), and 820 (s, para) cm^{-1}. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.14; H, 8.32.

1,2-Epoxy-5-*p*-tolylpentane (5b): bp 83–84 °C (0.6 mm); n^{22}_D 1.5112; NMR δ 1.2–2.1 (m, 4 H), 2.2–2.3 (m, 1 H overlapping $ArCH_3$), 2.3 (s, $ArCH_3$), 2.4–3.0 (m, 4 H), 7.0 (s, 4 ArH); IR (AgCl disks) 1260 (m, epoxide), 920 (m), and 810 (s, para) cm^{-1}. Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.88; H, 9.42.

1,2-Epoxy-5-phenylpentane (5c) was reported earlier.[1]

1,2-Epoxy-5-(*p*-fluorophenyl)pentane (5d): bp 64–65 °C (0.25 mm); n^{22}_D 1.4900; NMR (CCl_4) δ 1.3–2.0 (m, 4 H), 2.3–3.0 (m, 5 H), 6.7–7.3 (m, 4 ArH); IR (AgCl disks) 1220 (s), 920 (m), and 830 (s, para) cm^{-1}. Anal. Calcd for $C_{11}H_{13}FO$: C, 73.31; H, 7.27. Found: C, 73.46; H, 7.53.

1,2-Epoxy-5-(*p*-chlorophenyl)pentane (5e): bp 102–104 °C (0.4 mm); n^{25}_D 1.5261; NMR (CCl_4) δ 1.0–2.0 (m, 4 H), 2.2 (m, 1 H), 2.4–2.9 (m, 4 H), 7.1 (A_2B_2, 4 H); IR (AgCl disks) 1260 (m), 1090 (s), 1010 (s), 920 (s), and 830 (para) cm^{-1}. Anal. Calcd for $C_{11}H_{13}ClO$: C, 67.18; H, 6.66. Found: C, 67.29; H, 6.76.

1,2-Epoxy-5-[*p*-(trifluoromethyl)phenyl]pentane (5f): bp 93–94 °C (1.5 mm); n^{22}_D 1.4625; NMR (CCl_4) δ 1.2–2.2 (, 4 H), 2.2–2.5 (m, 1 H), 2.4–3.0 (m, 4 H), 7.2–7.7 (m, 4 ArH); IR (AgCl disks) 1110–1160 (s, CF_3), 810 (s, para) cm^{-1}: mass spectrum, exact mass m/e calcd for $C_{12}H_{11}F_3$ ($M^+ - H_2O$) 212.0812, found 212.0834.

7-Methoxy-1,2,3,4-tetrahydro-1-naphthalenemethanol (6a): bp 113–114 °C (0.05 mm); n^{25}_D 1.5557; NMR (CCl_4) δ 1.4–2.1 (m, 4 H), 2.7 (s, OH), 2.4–3.0 (m, 3 H), 3.6 (d, 2 H, J = 6.5 Hz), 3.7 (s, CH_3O), 6.4–7.0 (m, 3 ArH); IR (AgCl disks) 3200–3600 (OH), 1240 (s, ether), 1040 (s, OH), and 805 (1,2,4-trisubstituted-benzene) cm^{-1}. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.81; H, 8.14.

7-Methyl-1,2,3,4-tetrahydro-1-naphthalenemethanol (6b): bp 88–90 °C (0.1 mm); n^{24}_D 1.5526; NMR (CCl_4) δ 1.6 (s, 1 OH), 1.7–2.1 (m, 4 H), 2.3 (s, $ArCH_3$), 2.4–3.2 (m, 3 H), 3.6 (d, 2 H, J = 6.5 Hz), 6.7–7.0 (m, 3 ArH); IR (AgCl disks) 3200–3700 (OH), 1020 (OH), and 800 (s, 1,2,4-trisubstituted-benzene) cm^1. Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.51; H, 9.26.

1,2,3,4-Tetrahydro-1-naphthalenemethanol (6c) was reported earlier.[1]

7-Fluoro-1,2,3,4-tetrahydro-1-naphthalenemethanol (6d): bp 88–90 °C (0.1 mm); NMR (CCl_4) δ 1.3 (s, 1 OH), 1.6–2.1 (m, 4 H), 2.5–3.1 (m, 3 H), 3.7 (d, 2 H, J = 6 Hz), 6.7–7.3 (m, 3 ArH); IR (AgCl disks) 3200–3700 (OH), 1240 (s), 1030 (s, OH), and 810 (m, 1,2,4-trisubstituted-benzene) cm^{-1}; mass spectrum, exact mass m/e calcd for $C_{11}H_{13}FO$ 180.0952, found 180.0956.

7-Chloro-1,2,3,4-tetrahydro-1-naphthalenemethanol (6e): bp 130–132 °C (0.7 mm); n^{24}_D 1.5654; NMR (CCl_4) δ 1.5–2.1 (m, 4 H), 2.4–3.1 (m, 3 H), 3.3 (s, 1 OH), 3.5–3.8 (d, 2 H, J = 6.5 Hz), 6.8–7.3 (m, 3 H); IR (AgCl disks) 3200–3600 (s, br, OH), 1900, 1750, 860, and 800 (1,2,4-trisubstituted-benzene) cm^{-1}: mass spectrum, exact mass m/e calcd for $C_{11}H_{13}ClO$ 196.0654, found 196.0645.

7-(*p*-Trifluoromethyl)-1,2,3,4-tetrahydro-1-naphthalenemethanol (6f): bp 99–105 °C (0.6 mm); n^{24}_D 1.497; NMR (CCl_4)

(32) The rearrangement products could only be separated from the normal products by capillary GC (J & W 30-m DBWAX column). The amount given is the percent of rearrangement products relative to the normal products.

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δ 1.4–2.1 (m, 4 H), 2.1 (s, OH), 2.4–3.1 (m, 3 H), 3.7 (d, J = 7 Hz, 2 H), 7.0–7.7 (overlapping singlet and AB pattern, 3 H); IR (AgCl disks) 3200–3600, 1310 (s, CF_3), 1110 and 1155 (s, CF_3), 815 and 855 (m, 1,2,4-trisubstituted-benzene) cm^{-1}: mass spectrum, exact mass m/e calcd for $C_{12}H_{13}F_3O$ 230.0918, found 230.0907.

General Procedure for Kinetic Studies. A single stock solution of Lewis acid was prepared (for a series of kinetic studies) by dissolving 0.23 g of $SnCl_4$ in 150 mL of anhydrous CH_2Cl_2.[34] Generally, 12.5 mL of this solution was added under N_2 to a dry, preweighed reaction vial equipped with a septum, and 12.5 mL of dry CH_2Cl_2 was added to adjust solution concentrations to the desired values. A known quantity of *o*-dichlorobenzene was added as an internal standard.[35,36] The solution was cooled to −5 °C in a constant temperature bath. After determining the amount needed for kinetic runs, the epoxide was added (twenty times the number of moles of $SnCl_4$),[36] and the vial was shaken rapidly and then vibrated gently throughout the reaction. Aliquots of the solution were removed by syringe[37] and quenched in aqueous saturated NaCl. A portion of the organic layer was injected into a Hewlett-Packard 5712 GC equipped with a 4 ft × $^1/_8$ in. 5% OV 101 column (temperature programming was used) and an integrator/recorder, and the extent of reaction was determined by integrator areas and the area/weight ratios of the alcohol and *o*-dichlorobenzene. The reactions were followed to >90% completion.[21] Data reduction and determination of pseudo-first-order rate constants were done by methods described by DeHaan.[38]

(1*R,4a*R*,4a*R*,8a*R*)-Decahydro-4-phenyl-1-naphthol.** In dried apparatus under N_2, a 0.31-g sample of *trans*-5,6-epoxy-*cis*-cyclodecene[17] (2 mmol) in 10 mL of dry CH_2Cl_2 was added over 15 min to a solution of dry benzene (23 g), 0.003 g of $SnCl_4$ (.01 mmol), and 20 mL of CH_2Cl_2 held at 0 °C. After 1 h, the solution was stirred at room temperature for 1 h and quenched with 5% $NaHCO_3$ and worked up as usual.[1] After solvent evaporation, the crystals formed (0.31 g, 71% pure by GC) were recrystallized from toluene/hexane: mp 119–120 °C (0.217 g, 70%);[34] NMR ($CDCl_3$) δ 7.2 (s, 5 ArH), 3.9 (td, 1 H), 2.8 (dt, 1 H), 0.8–2.4 (m, 15 H); IR (KBr) 3200–3600 (s, OH), 1040 (s, OH), 735 and 690 (monosubstituted-benzene) cm^{-1}. Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.13; H, 10.00.

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(34) This solution was kept under N_2 in a dessicator and was removed via a septum by syringe techniques.
(35) Chosen because of its inertness to the reaction conditions and its GC retention time. Generally, the weight ratio of *o*-dichlorobenzene to epoxide was 2:1.
(36) The weights of each substance added was determined by preweighing a filled syringe, adding the compounds, via syringe, and reweighing the emptied syringe. The volumes of compounds added, and their densities, were measured also to provide a check on the weights.
(37) The syringes were kept at −5 °C by submerging them in dry CH_2Cl_2 in the kinetics constant temperature bath.
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Mechanistic Investigations of the Cycloaddition Reactions of Thioxanthenylidene *S*,*S*-Dioxide

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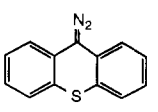
Photolysis of 9-diazothioxanthene *S*,*S*-dioxide (**9**) in the presence of the substituted styrenes **11–15** gave the corresponding spirocyclopropane adducts **18–22** in high yield (67–86%), in addition to minor amounts of bi-9,9′-thioxanthenylidene *S*,*S*,*S*′,*S*′-tetroxide (**10**). Laser flash photolysis of **9** produced a transient absorption (λ_{max} 324 nm) which was efficiently quenched by oxygen and was assigned to the carbene **2**. This species was quenched by alcohols in a fast reaction attributable to the singlet state of **2**, and in acetonitrile an ylide (**24**) was obtained. Quenching of **2** with the styrenes allowed the determination of the absolute rate constants for these reactions. The reactive spin state of **2** was investigated by studying the stereochemistry of the (1 + 2) cycloaddition of the carbene with *trans*-β-methylstyrene.

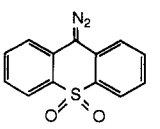
Introduction

The reactions of sulfur-containing carbenes (Scheme I) with olefins have been the subject of several previous studies which have suggested that significant interactions occur between the carbene center and the sulfur atom.[1-7] Of special interest are the results of Dürr[6] and Patrick[7] concerning thioxanthenylidene (**1**) and thioxanthenylidene S,S-dioxide (**2**).

Dürr found that photolysis of 9-diazothioxanthene (**3**), the precursor of **1**, in the presence of tri- and tetramethylethylene gives no addition or insertion products.[6]



3



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Dithioxanthene (**4**) and thioxanthone (**5**) were the main

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