126–129 °C dec; ^{1}H NMR (CD_3OD) δ 2.30 (s, 2.8 H), 6.57 (dd, 1.1 H), 6.97–8.13 (m, 10.1 H).

Anal. Calcd for $C_{17}H_{14}FISO_4$: C, 44.36; H, 3.07; I, 27.57. Found: C, 44.52; H, 3.02; I, 27.70.

(4-Fluorophenyl)(2-furyl)iodonium tosylate: from 2-lithiofuran (20 mmol) and (*tert*-butylethynyl)(4-fluorophenyl)-iodonium tosylate (3.80 g, 8.01 mmol); yield, 1.20 g (32.5%); mp 136–138 °C dec; ^{1}H NMR (CD_3OD) δ 2.32 (s, 2.9 H), 6.53 (dd, 1.0 H), 6.93–8.33 (m, 10.2 H, includes obvious low field m at δ 8.12 (2.1 H)).

Anal. Calcd for $C_{17}H_{14}FISO_4$: C, 44.36; H, 3.07; I, 27.57. Found: C, 44.55; H, 3.29; I, 27.67.

(3-Chlorophenyl)(2-furyl)iodonium tosylate: from 2-lithiofuran (20 mmol) and (*tert*-butylethynyl)(3-chlorophenyl)-iodonium tosylate (3.92 g, 7.99 mmol); yield, 0.79 g (21%); mp 114–116 °C dec; ^{1}H NMR (CD_3OD) δ 2.31 (s, 2.9 H), 6.56 (dd, 1.0 H), 6.93–8.36 (m, 10.2 H).

Anal. Calcd for $C_{17}H_{14}ClISO_4$: C, 42.83; H, 2.96; I, 26.62. Found: C, 42.80; H, 2.96; I, 26.77.

(2-Methylphenyl)(2-thienyl)iodonium tosylate: from 2-lithiothiophene (10 mmol) and (*tert*-butylethynyl)(2-methylphenyl)iodonium tosylate (0.94 g, 2.0 mmol); yield, 0.59 g (62.5%); mp 116–118 °C dec [lit.[8] mp 144–148 °C]; ^{1}H NMR (CD_3OD) δ 2.28 (s, 2.8 H), 2.63 (s, 2.9 H), 6.92–8.38 (m, 11.2 H, includes d at δ 8.20 (1.0 H)).

(2-Methylphenyl)(5-methyl-2-thienyl)iodonium tosylate: from 2-lithio-5-methylthiophene (10 mmol) and (*tert*-butylethynyl)(2-methylphenyl)iodonium tosylate (0.94 g, 2.0 mmol); yield, 0.62 g (64%); mp 123–125 °C dec [lit.[8] mp 132–133 °C dec]; ^{1}H NMR (CD_3OD) δ 2.28 (s, 2.8 H), 2.48 (s, 2.7 H), 2.62 (s, 3.4 H), 6.71 (m, 1.0 H), 6.94–7.81 (m, 8.0 H), 8.18 (d, 1.0 H).

Phenyl(2-thianaphthenyl)iodonium Tosylate. To a solution of *n*-butyllithium (11.0 mmol, 2.4 M solution in hexane) in Et_2O (20 mL), kept under nitrogen and chilled in an ice/salt bath, was added, dropwise and with stirring, a solution of thianaphthene (1.34 g, 9.99 mmol) in Et_2O (5 mL). After 20 min, solid (*tert*-butylethynyl)phenyliodonium tosylate (1.82 g, 3.99 mmol) was introduced under a positive nitrogen pressure. The reaction mixture was stirred for 30 min, during which time it became less heterogeneous and turned slightly red in color, and was then treated with a solution of *p*-TsOH·H_2O in Et_2O (ca. 0.22 M, 70 mL) whereupon additional white solids separated. The mixture was allowed to warm to room temperature, and the solids were isolated, washed with Et_2O, and triturated for 15 min with H_2O (100 mL). The water insoluble, white crystals of phenyl(2-thianaphthenyl)iodonium tosylate were isolated, washed with H_2O, and dried in vacuo over P_2O_5: yield, 1.43 g (70.5%); mp 158–160 °C dec; ^{1}H NMR (Me_2SO-d_6) δ 2.25 (s, 2.9 H), 6.87–8.57 (m, 14.1 H).

Anal. Calcd for $C_{21}H_{17}IS_2O_3$: C, 49.61; H, 3.37; I, 24.96. Found: C, 49.55; H, 3.52; I, 25.07.

Phenyl(2-furyl)iodonium Iodide. To a mixture of phenyl(phenylethynyl)iodonium tosylate (0.70 g, 1.47 mmol) and Et_2O (25 mL), kept under nitrogen and cooled in a dry ice/acetone bath, was added with stirring a mixture of 2-lithiofuran (12.0 mmol) in Et_2O/hexane. After 4 h, the reaction mixture was warmed to −10 °C, kept at that temperature for 30 min, and subsequently allowed to warm to room temperature whereupon it became less heterogeneous and acquired a light red color. A saturated solution of HCl in Et_2O (10 mL) was then added, and a dark solid separated. The solids were isolated and treated with cold H_2O (150 mL), and the mixture was filtered (to remove solid impurities) into an aqueous solution of KI. Phenyl(2-furyl)iodonium iodide precipitated (yellow solid) and was isolated, washed with Et_2O, and dried in air: yield, 0.35 g (60%); mp 125–126 °C dec; ^{1}H NMR (Me_2SO-d_6) δ 6.60 (dd, 1.1 H), 6.85–7.68 (m, 4.0 H), 7.93 and 8.15 (m and d of m, 2.9 H).

Anal. Calcd for $C_{10}H_8I_2O$: C, 30.18; H, 2.03; I, 63.77. Found: C, 30.45; H, 2.10; I, 63.84.

Acknowledgment. We thank the Dow Chemical Company for their financial support of this work.

Registry No. 1 (R = H), 92473-47-7; 1 (R = 2-Me), 92543-63-0; 1 (R = 3-Me), 92543-61-8; 1 (R = 4-Me), 92543-49-2; 1 (R = 2-F), 92543-51-6; 1 (R = 3-F), 92543-53-8; 1 (R = 4-F), 92543-55-0; 1 (R = 3-Cl), 92543-57-2; 1 (R = 4-Cl), 92543-59-4; 2 (R = 2-Me), 85925-51-5; 2 (R = 3-Me), 85925-53-7; 2 (R = 4-Me), 85925-55-9; 2 (R = 2-F), 92575-11-6; 2 (R = 3-F), 92543-65-2; 2 (R = 4-F), 85925-57-1; 2 (R = 3-Cl), 92543-67-4; 5 (R = H), 27126-76-7; 5 (R = 2-Me), 73177-97-6; 5 (R = 3-Me), 92543-47-0; 5 (R = 4-Me), 73177-96-5; 5 (R = 2-F), 84383-95-9; 5 (R = 3-F), 84383-96-0; 5 (R = 4-F), 84383-77-7; 5 (R = 3-Cl), 84383-84-6; 5 (R = 4-Cl), 73178-07-1; 3,3-dimethyl-1-butyne, 917-92-0; phenyl(phenylethynyl)iodonium tosylate, 79069-32-2; phenylacetylene, 536-74-3; furan, 110-00-9; (2-methylphenyl)(2-thienyl)iodonium tosylate, 91228-43-2; thiophene, 110-02-1; 2-methylthiophene, 554-14-3; (2-methylphenyl)(5-methyl-2-thienyl)iodonium tosylate, 91228-56-7; phenyl(2-thianaphthenyl)iodonium tosylate, 92543-69-6; thianaphthene, 95-15-8; phenyl(2-furyl)iodonium iodide, 92543-70-9.

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Nucleophilic Participation of Phenyl in the Ring-Opening Reactions of *cis*- and *trans*-2,3-Dibenzyloxirane

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Methanolysis reactions of both epoxides *cis*-**4** and *trans*-**5** under different conditions are completely anti stereoselective, no trace of the products arising from syn opening being found. Also the hydrolysis, the acetolysis, and the trichloroacetolysis in non-protic solvents of **4** are completely anti stereoselective, whereas the corresponding reactions of **5** yield nonnegligible amounts of syn adducts, which in some trichloroacetolysis reactions reach 21.7%. These data suggest that some of the openings of the trans epoxide **5** occur in part through nucleophilic participation of phenyl, whereas the reactions of the cis isomer **4** exhibit no such participation. The markedly lower capability of **4** to give phenyl participation may be due to the severe steric interactions which arise in the formation of the phenonium-type species from cis epoxide **4**.

It is well established that the stereochemistry of ring opening of oxiranes bearing neither aryl nor other unsaturated systems directly linked to the ring under acidic conditions is essentially anti.[1-3] However, when aryls or other unsaturated systems are present on the oxirane ring, the observed stereochemistry of the ring opening can range

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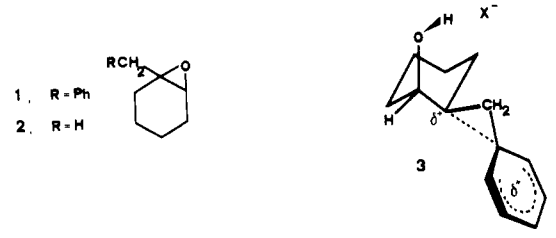
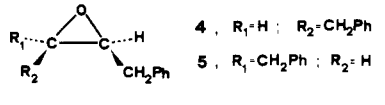
(2) Buchanan, J. G.; Sable, H. Z. In "Selective Organic Transformations"; Thyagarajan, B. S., Ed.; Wiley-Interscience: New York, 1972; Vol. 1, p 1.

0022-3263/84/1949-4706$01.50/0

from complete retention to complete inversion, depending on the structure of the epoxide and on the reaction conditions in general.[1,2,4,5] The amount of syn addition observed was found to be directly linked to the capability of the aryl or of the other substituents to stabilize the intermediate carbocationic species formed at the time of breaking of the C–O bond of the protonated oxirane.[4,5] Recently in connection with our studies on the mechanism and the stereochemistry of reactions of 1,2-epoxides bearing "particular substituents" bonded to the ring, we extended our research to 2-benzyloxiranes[6] in order to evaluate the possibility of neighboring group participation by a phenyl, not directly linked to the oxirane ring, in ring-opening reactions. The insertion of a methylene group between the aryl and the oxirane carbon, as in 2-benzyloxiranes, inhibits mesomeric interaction between the aromatic ring and the carbocationic center formed in the ring-opening process.[2,4] Apart from the possibility of nucleophilic aryl participation in the ring-opening process of 2-benzyloxiranes, the aryl group should exert only a weak electron-withdrawing inductive effective[7] through the methylene bridge.

Even if the phenomenon of aryl participation has been reasonably suggested and demonstrated for solvolysis of β-arylalkyl systems, it has not yet been conclusively proved in the ring opening of oxiranes. Some evidence for such participation was obtained in acid-catalyzed ring-opening reactions of 1-benzyl-1,2-epoxycyclohexane (1).[6] In particular, the formation of significant amounts of syn products in these reactions markedly higher than that observed in the reactions of the corresponding methyl-substituted oxirane (2), strongly suggested aryl participation. The formation of syn products was rationalized[6] through the intermediacy of phenonium-type species of type 3. However, the noncomplete regiospecificity of the reactions of 1 prevented quantitative approaches to the study of nucleophilic assistance by phenyl, and more generally by aryl groups, in the ring-opening process of 2-benzyloxiranes. Our studies on this topic have been extended to *cis*- (4) and *trans*-2,3-dibenzyloxirane (5) in which the equivalence





4, R_1=H; R_2=CH_2Ph

5, R_1=CH_2Ph; R_2=H

of the two epoxidic carbons should facilitate stereochemical study of the ring opening of these epoxides and consequently of aryl participation, because of the absence of regioselectivity problems. Furthermore, these substrates should give information on the dependence of the steric course of ring opening, and therefore of aryl participation, on configuration of the starting epoxide.

Table I. Product Composition in the Ring-Opening Reactions of Epoxides *cis*-4 and *trans*-5 in Acidic Methanol

reagents		4		5	
		syn adduct[a]	anti adduct[b]	syn adduct[b]	anti adduct[a]
MeOH	H_2SO_4	0	100	0	100
MeOH–$LiClO_4$[c]	TsOH	0	100	0	100
MeOH–CH_2Cl_2[d]	TsOH	0	100	0	100

[a] *pref*-Methoxy alcohol 11. [b] *parf*-Methoxy alcohol 10. [c] 0.5 M solution in $LiClO_4$. [d] Molar ratio of epoxide/acid/MeOH of 1:0.1:6.

Results

Epoxides *cis*-4 and *trans*-5 were obtained from the corresponding olefins of known configuration, 6[8] and 7[9], respectively, by direct epoxidation with *m*-chloroperoxybenzoic acid. Pure trans olefin 7 was prepared by treatment of *trans,trans*-1,4-diphenyl-1,3-butadiene with sodium in moist ether in a modification of the Straus method;[9a] the cis isomer 6 was obtained, accompanied by small amounts (11%) of the trans isomer 7, by Wittig reaction of phenylacetaldehyde with the ylide derived from the (2-phenylethyl)triphenylphosphonium bromide.[8] Pure cis olefin 6 was obtained by column chromatography on 15% $AgNO_3/SiO_2$.

The ring-opening reactions of both the cis (4) and the trans epoxide (5) under acidic conditions were carried out under the same conditions under which 2-benzyloxirane (1) was studied, that is, acid hydrolysis and methanolysis under different conditions, acetolysis, and trichloroacetolysis in several aprotic solvents. The mixtures of diols 8 and 9 (hydrolysis reaction) and of the methoxy alcohols 10 and 11 obtained were analyzed directly by GLC. In the case of the acetolyses and of the trichloroacetolyses the reaction mixtures were analyzed after saponification of the monoesters obtained. The results are shown in Tables I and II.

The stereochemistry of the products obtained in the ring-opening reactions of epoxides 4 and 5 could not have been firmly established on the basis of the usual anti stereoselectivity in the acid-catalyzed ring opening of oxiranes because of the possibility of phenyl participation in the ring-opening processes, which could have substantially modified the stereochemical results.[6] The relative configurations of the diols 8 and 9, and of the methoxy alcohols 10 and 11, have been inferred through unequivocal stereospecific synthesis. Cis dihydroxylation of the cis (6) and trans olefin (7) with OsO_4[10] afforded stereospecifically the meso (8) and the *d,l* diol (9), respectively. On the other hand, the configurations of the *parf*[11] 10 and of the *pref*[11] methoxy alcohol 11 were defined by their stereospecific formation in the base-catalyzed methanolysis of the cis (4)

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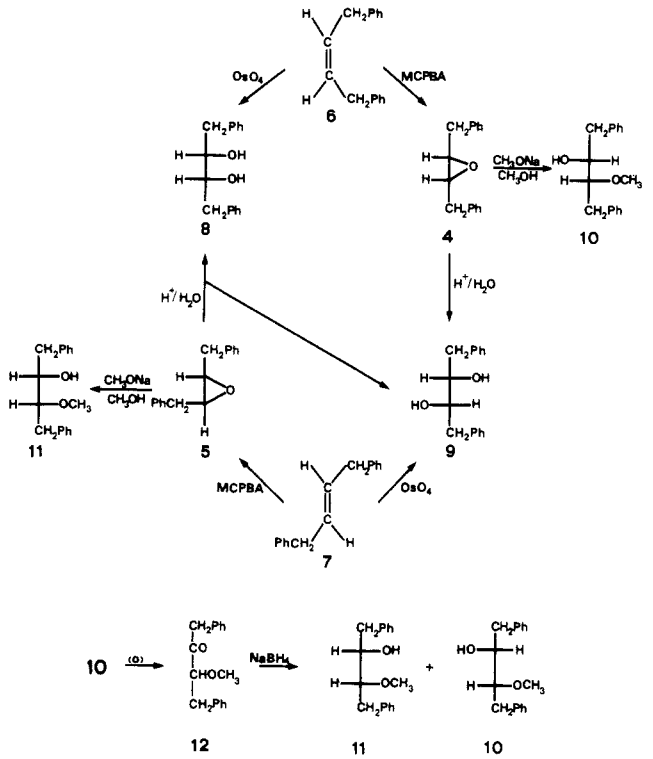
(9) (a) Straus, F. *Liebigs Ann. Chem.* **1905**, *342*, 190. (b) Blum, J.; Becker, Y. *J. Chem. Soc., Perkin Trans. 2*, **1972**, 982.
(10) Schroder, M. *Chem. Rev.* **1980**, *80*, 187.
(11) The proposal of F. A. Carey and M. E. Kuehne for specifying relative configuration in molecules with multiple chiral centers has been adopted in order to avoid the ambiguous descriptors erythro and threo; see: Carey, F. A.; Kuehne, M. E. *J. Org. Chem.* **1982**, *47*, 3812.

Table II. Product Composition in the Hydrolysis, Trichloroacetolysis, and Acetolysis of Epoxides *cis*-4 and *trans*-5

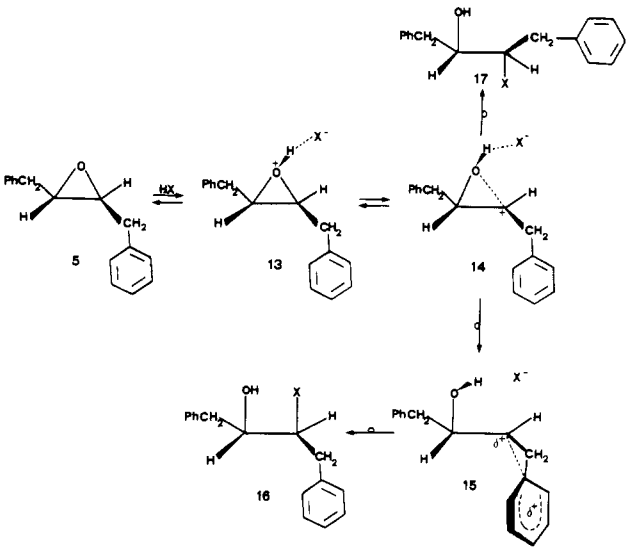
reagents		4		5	
		syn adduct[a]	anti adduct[b]	syn adduct[b]	anti adduct[a]
H_2O	H_2SO_4	0	100	11.5	88.5
cyclohexane	CCl_3COOH[c]	0	100	2.2	97.8
CCl_4	CCl_3COOH[c]	0	100	3.0	97.0
benzene	CCl_3COOH[c]	0	100	8.4	91.6
$CHCl_3$	CCl_3COOH[c]	0	100	8.6	91.4
CH_2Cl_2	CCl_3COOH[c]	0	100	21.7	78.3
CH_3COOH	TsOH[c]	0	100	5.0	95.0

[a] Meso diol 8. [b] *d,l* diol 9. [c] After saponification of the crude reaction mixture.

Scheme I



Scheme II

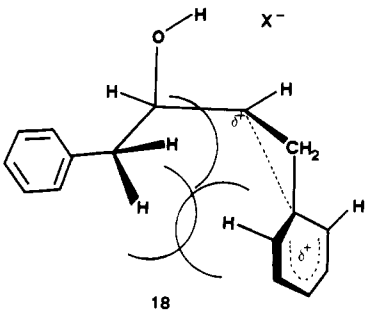


and of the trans epoxide (**5**), respectively, in accordance with S_N2-type substitution in the ring opening of oxiranes under strongly basic conditions.[1,2,4d,12] On the other hand, the diastereoisomeric nature of **10** and **11** was proved by oxidation of **10** to the ketone **12** whose reduction afforded a mixture of **10** and **11** (see Scheme I).

Discussion

All the methanolysis reactions of both the epoxides **4** and **5** are completely anti stereoselective, no trace of the products arising from syn opening being found. Also the hydrolysis, the acetolysis, and the trichloroacetolyses in non-protic solvents of the cis epoxide **4** are completely anti stereoselective (see Table I), whereas the corresponding reactions of the trans epoxide **5** show the presence of nonnegligible amounts of syn adducts, which in some trichloroacetolysis reactions reach significant values (see Table II). These data suggest that some of the openings of the trans epoxide **5** occur in part through nucleophilic participation of phenyl, whereas the reactions of the corresponding cis epoxide **4** exhibit absolutely no participation by phenyl. In other words, the cis epoxide **4** is considerably less liable to phenyl participation than the trans form **5**. The ring-opening process under acidic conditions can be well accounted for through a mechanism (see Scheme II) analogous to the one previously suggested for the benzyloxirane **1**,[6] which implies neighboring aryl participation, to a certain degree, at the β oxirane carbon in the intramolecular intimate ion–dipole pair **14** (successive to the protonated oxirane **13**), and formation of a discrete, but unsymmetrically bridged phenonium ion **15**, which on attack of the nucleophile affords the syn adduct **16**. Direct attack of the nucleophile on **14** would give the anti adduct **17**.

The markedly lower capability of the cis epoxide **4** to give phenyl participation could be due to the severe steric interactions which arise during formation of the phenonium ion type species **18** from the cis epoxide **4**, between



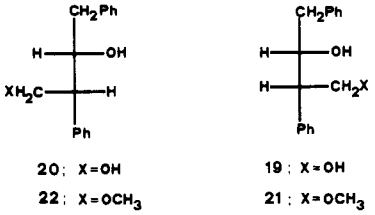
18

one of the ortho hydrogens of the neighboring phenyl and the methylene hydrogens of the other benzyl group, as can be shown by molecular models. These data seem to confirm[6] that phenyl participation occurs in carbocationic species, originating from the protonated oxirane **13**, either which have not lost the memory of the former oxirane C–O bond or in which there is still an interaction between the former oxirane carbon and oxygen (**14**), such as not to allow substantial conformational changes around the former

(12) Brewster, J. H. *J. Am. Chem. Soc.* **1956**, *78*, 4061.

oxirane C–C bond (see Scheme II).

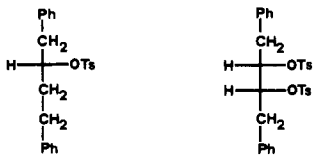
None of the above-mentioned reactions of the epoxides **4** and **5** revealed even in trace the presence of rearrangement products *pref*[11]-**19** and *parf*[11]-**20** and *pref*[11]-**21** and *parf*[11]-**22**,[13] which might have arisen from attack of the



20: X=OH **19**: X=OH
22: X=OCH_3 **21**: X=OCH_3

nucleophile on the less substituted carbon of the intermediate phenonium ion of type **18** and **15**. Such a type of unusual rearrangement of an aryl group from the less substituted carbon to the more substituted one[14] could have been expected on the basis of previous results obtained by Dubois[15] in the aryl-assisted solvolysis of β-aryl substrates possessing electron-withdrawing substituents beside the leaving group[15a] and in the aryl-assisted bromination of 3-arylpropenes.[15b]

Somewhat surprisingly, the degree of aryl participation even in ring opening of the trans oxirane **5** is not markedly high. Secondary β-aryl substrates are considered to react via neighboring group participation in substantial amount.[8,16,17] The aryl-assisted pathway in acetolysis of 1,4-diphenyl-2-butyl tosylate (**23**) occurs to the extent of



23 **24**

some 35%.[8,17] Furthermore, the presence of an electron-withdrawing group on a carbon adjacent to the reaction center increases the electron demand at the reactive site requiring greater aryl participation;[9,17] the aryl participation calculated for the acetolysis of the ditosylate **24**, in which a second tosylate group has been introduced in the 3 position of **23**, is drastically increased to 94%.[8,17] Keeping in mind that solvolysis of tosylates and acid-catalyzed ring-opening reactions are completely different reactions, however, the acetolyses of epoxide **4** and **5** and that of the structurally strictly related ditosylates of the meso diol **8** (**24**) should lead to intermediates structurally and electronically quite similar. The large differences observed in the participation of the phenyl between the acetolyses of **4** and **5** and that of **24** appear at this moment not completely understandable. Unfortunately, the data for solvolysis of the ditosylate of the *d,l* diol **9** have not been reported.[8,17]

As for the differences in stereoselectivity and therefore in the aryl participation of the ring opening of the trans epoxide **5** under different conditions, an analogous trend has been observed in the ring-opening reactions of the benzyloxirane **1**.[6]

Experimental Section

Melting points were determined on a Kofler apparatus and are uncorrected. IR spectra for comparison between compounds were taken in paraffin oil mulls on a Perkin-Elmer Model 137 Infracord. ^1H NMR spectra were determined in 10% $CDCl_3$ solution with a Varian EM 360 spectrometer using Me_4Si as an internal standard. GLC analyses of the mixtures of diols **8** and **9** (detected as trimethylsilyl derivatives) were run on a Carlo Erba Fractovap 2300 apparatus with a flame ionization detector with glass column (2 m × 2.5 mm) packed with 10% diethylene glycol succinate on 80–100-mesh silanized Chromosorb W [column: low isotherm 155 °C (21 min), high isotherm 170 °C, increasing temperature 3 °C/min; evaporator and detector 250 °C; nitrogen flow 30 mL/min]; the order of increasing retention times was **9** < **8**. GLC analyses of the mixtures of methoxy alcohols **10** and **11** were determined on the same apparatus described above, but with column of 1.5 m × 2.5 mm and under the following conditions: column 210 °C, evaporator and detector 275 °C, nitrogen flow 30 mL/min; the order of increasing retention times was **10** < **11**. The crude reaction mixtures from methanolysis, hydrolysis, and trichloroacetolysis of epoxides **4** and **5** were run also on a Dani Gas cromatograph 3800 apparatus with a flame ionization detector with SE 52 capillary glass column (20 m × 0.2 mm) (column 200 °C, evaporator and detector 230 °C, nitrogen flow 2 mL/min), in order to verify the eventual presence in such mixtures of the rearranged products **19** and **20** (hydrolysis and trichloroacetolysis) and **21** and **22** (methanolysis) (see Discussion above).[13] Preparative TLC was performed on 2-mm-layer silica gel plates (Merck F_{254}) containing a fluorescent indicator. All comparisons between compounds were made on the basis of IR and NMR spectra and GLC. Magnesium sulfate was always used as the drying agent. Petroleum ether refers to the fraction bp 40–70 °C. Evaporations were done in vacuo (rotating evaporator). Cyclohexane, CCl_4, $CHCl_3$, and CH_2Cl_2 were refluxed over P_2O_5 and rectified. Benzene was washed with concentrated sulfuric acid, kept at reflux over sodium, and distilled.

***cis*-1,4-Diphenyl-2-butene (6)** was prepared as previously described[8] by Wittig reaction between phenylacetaldehyde (7.64 g, 0.063 mol) and the ylide derived from (2-phenylethyl)triphenylphosphonium bromide (35.6 g, 0.079 mol) by butyllithium (50 mL of a 1.6 M solution). The crude reaction product was dissolved in petroleum ether and filtered through a short Al_2O_3 column, eluting with petroleum ether. The eluent solvent (200 mL) was evaporated and the residue was chromatographed through a 15% $AgNO_3/SiO_2$ (200 g) column: elution with a 95:5 mixture of petroleum ether and ether afforded olefin *trans*-**7** (0.80 g) and successive elution with ether afforded pure olefin *cis*-**6** (9.4 g).

***trans*-1,4-Diphenyl-2-butene (7).** Metallic Na (5.0 g) was slowly added to a stirred solution of *trans,trans*-1,4-diphenyl-1,3-butadiene (6.0 g) in moist ether (600 mL). After 24 h, more Na and more drops of water were alternatively added to the stirred reaction mixture in order to maintain a good evolution of hydrogen; when TLC analysis showed no more the presence of the diene, the ether solution was decanted, dried, and evaporated to dryness to give a liquid (5.6 g) which solidifies on cooling. Recrystallization from EtOH gave pure **7** (3.5 g): mp 43–45 °C (lit.[9b] mp 45.5–46 °C).

***meso*-1,4-Diphenyl-2,3-butanediol (8).** OsO_4 (0.010 g) in *tert*-butyl alcohol (0.6 mL) was added to a stirred mixture of *N*-methylmorpholine *N*-oxide·H_2O (0.909 g, 6.72 mmol) in water (2.8 mL) and acetone (1.8 mL); **6** (1.2 g, 5.76 mmol) was then added under nitrogen and the resulting mixture was maintained at room temperature with a water bath for 1 h and then stirred overnight at room temperature. After this time, the reaction mixture was treated with a slurry of $NaHSO_3$ (0.10 g) and magnesium silicate (0.70 g) in water (5 mL); after 2 h of vigorous stirring, the silicate was filtered and the residue washed with ether. The combined filtrate was acidified with 1 N H_2SO_4 at pH 2 and extracted with ether. Evaporation of the washed (saturated aqueous $NaHCO_3$ and water) and dried, ether extracts yielded a solid residue (0.15 g) which on recrystallization from petroleum ether and few drops

(13) The complete experimental details of the preparation and the configurational study of the rearrangement compounds **19–22** will be reported in a forthcoming paper.
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of acetone afforded pure **8** (0.060 g): mp 139–140 °C (lit.[18] mp 137–138 °C).

***d,l*-1,4-Diphenyl-2,3-butanediol (9).** Analogous treatment of trans olefin **7**, as described for **6**, afforded pure **9** (0.050 g), after recrystallization from petroleum ether and a few drops of acetone: mp 126–128 °C (lit.[18] mp 123–126 °C).

***cis*-2,3-Dibenzyloxirane (4).** A cooled solution (−20 °C) of **6** (0.70 g, 3.36 mmol) in $CHCl_3$ (20 mL) was treated portionwise under stirring with 90% *m*-chloroperoxybenzoic acid (MCPBA) (0.705 g, 3.69 mmol). After the addition was completed, the reaction mixture was stirred for 1 h at −20 °C and then left 24 h at 5 °C. Evaporation of the washed (saturated aqueous $NaHCO_3$ and water) and filtered organic solution yielded a liquid residue (0.68 g) consisting of impure **4** which was filtered through a silica gel column (5 cm × 1.5 cm), eluting with petroleum ether and collecting fractions of about 30 mL: fractions 2 and 3 afforded pure **4** (0.35 g) as a solid: mp 31–33 °C; NMR δ 3.25 (m, 2, 
CH-HC), 3.00 [m, 4, $(PhCH_2)_2$]. Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.89; H, 7.05.

***trans*-2,3-Dibenzyloxirane (5).** Analogous treatment of trans olefin **7** (1.39 g, 6.68 mmol) in $CHCl_3$ (30 mL) with 90% MCPBA (1.4 g, 7.35 mmol) afforded a crude liquid product (1.20 g) which was filtered through a silica gel column (5 cm × 1.5 cm), eluting with petroleum ether and collecting fractions of about 30 mL. Fractions 1 and 2 afforded pure **5** (0.97 g) as a liquid: NMR δ 2.95 [m, 6, $(PhCH_2CH)_2$]. Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.65; H, 7.35.

Reaction of Epoxide 5 with Trichloroacetic Acid in Anhydrous Benzene. A solution of epoxide **5** (0.530 g, 2.36 mmol) in anhydrous benzene (50 mL) was treated with 1 N CCl_3COOH solution in anhydrous benzene (2.59 mmol) and resulting reaction mixture was left 2 days at room temperature. Evaporation of the washed (saturated aqueous $NaHCO_3$ and water) and dried organic solution afforded a liquid residue (0.65 g) which was dissolved in THF (40 mL) and treated with 1 M KOH in ethanol (12.5 mL); after 4 h at room temperature, water was added and the resulting mixture was extracted with ether. Evaporation of the washed (water) and dried ether extracts afforded a solid residue (0.48 g) which was recrystallized from petroleum ether and acetone (few drops) to give pure **8** (0.25 g).

Reaction of Epoxide 4 with Trichloroacetic Acid in Anhydrous Benzene. A solution of epoxide **4** (0.10 g, 0.44 mmol) was treated with 1 N CCl_3COOH solution in anhydrous benzene (0.48 mL), as described above for the corresponding reaction of epoxide **5**, to give, after saponification, a crude reaction product (0.080 g) consisting of **9**. Recrystallization from petroleum ether and acetone (few drops) afforded pure **9** (0.030 g).

Reaction of Epoxide 5 with 0.2 N H_2SO_4. A suspenstion of epoxide **5** (0.15 g) in 0.2 N H_2SO_4 (15 mL) was stirred at 50 °C for 24 h. After cooling, solid $NaHCO_3$ was added, and the resulting mixture was extracted with ether; evaporation of the washed (water) and dried ether extracts afforded a solid residue (0.14 g) which was recrystallized from petroleum ether and acetone (few drops) to give pure **8** (0.060 g).

When the same reaction was repeated at room temperature, a small amount of addition product was recovered together with the unreacted starting epoxide.

Reaction of Epoxide 4 with 0.2 N H_2SO_4. Analogous treatment of epoxide **4** (0.10 g) with 0.2 N H_2SO_4 (10 mL) at 50 °C for 24 h afforded a crude reaction product (0.095 g) consisting of **9**. Recrystallization from petroleum ether and acetone (few drops) afforded pure **9** (0.045 g). When the same reaction was repeated at room temperature, a small amount of addition product was recovered together with the unreacted starting material.

***parf*-3-Methoxy-1,4-diphenyl-2-butanol (10).** Cis epoxide **4** (0.15 g) in anhydrous methanol (5 mL) was slowly added to a stirred solution of MeONa (from 1.5 g of Na) in anhydrous methanol (20 mL); the resulting mixture was refluxed 24 h, then cooled, diluted with water, and extracted with ether. Evaporation of the washed (water) and dried ether extracts yielded a liquid residue (0.12 g), mostly consisting of hydroxy ether **10**, which was subjected to semipreparative TLC on 0.5-mm silica gel plates (a 85:15 mixture of petroleum ether and ether was used as the eluent; elution was repeated 3 times). Extraction of the most intense band (R_f 0.55) afforded pure **10** (0.060 g) (GLC) as a liquid: IR λ 2.92 μm (OH); NMR δ 4.40 (q, 1, $CHOCH_3$), 3.70 (m, 1, CHOH), 3.28 (s, 3, OCH_3). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.95; H, 7.52.

***pref*-3-Methoxy-1,4-diphenyl-2-butanol (11).** Analogous treatment of trans epoxide **5** (0.15 g), as described above for **4**, afforded a liquid residue (0.11 g), mostly consisting of hydroxy ether **11**, which was purified by semipreparative TLC on 0.5-mm silica gel plates (a 85:15 mixture of petroleum ether and ether was used as the eluent; elution was repeated 3 times). Extraction of the most intense band (R_f 0.52) afforded pure **10** (0.070 g) (GLC) as a liquid: IR λ 2.94 μm (OH); NMR δ 4.43 (q, 1, $CHOCH_3$), 3.80 (m, 1, CHOH), 3.21 (s, 3, OCH_3). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.42; H, 7.62.

Reaction of Epoxide 4 with 0.2 N H_2SO_4 in Anhydrous Methanol. Epoxide **4** (0.40 g) was added to a 0.2 N H_2SO_4 solution in anhydrous MeOH (40 mL) and the resulting reaction mixture was stirred 24 h at room temperature. Water was added and the suspension extracted with ether; evaporation of the washed (saturated aqueous $NaHCO_3$ and water) and dried ether extracts afforded pure **10** (0.35 g) (GLC).

Reaction of Epoxide 5 with 0.2 N H_2SO_4 in Anhydrous Methanol. Analogous treatment of epoxide **5** (0.10 g) with 0.2 N H_2SO_4–MeOH solution (10 mL) afforded a liquid residue (0.080 g) consisting of pure **11** (GLC).

1,4-Diphenyl-3-methoxy-2-butanone (12). A solution of hydroxy ether **10** (0.22 g, 0.86 mmol) in acetone (20 mL) was treated dropwise under stirring with Jones reagent[19] (0.23 mL) at room temperature. After 10 min the reaction mixture was diluted with water and extracted with ether; evaporation of the washed (water, 10% aqueous Na_2CO_3, and water) and dried ether extracts yielded a liquid residue (0.18 g) consisting of pure **12** (GLC): IR λ 5.82 μm (C=O); NMR δ 3.90 (m, 1, $CHOCH_3$), 3.67 (s, 2, CH_2CO), 3.23 (s, 3, OCH_3), 2.90 (d, 2, J = 5.8 Hz, $PhCH_2$). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.00; H, 7.29.

Reduction of 12 with $NaBH_4$. A solution of **12** (0.18 g, 0.71 mmol) in 95% EtOH (16 mL) was treated with $NaBH_4$ (0.30 g, 8.1 mmol) and stirred at room temperature for 3 h. The reaction mixture was acidified with 2 N H_2SO_4, diluted with water, and extracted with ether. Evaporation of the washed (saturated aqueous $NaHCO_3$ and water) and dried ether extracts gave a residue (0.14 g) consisting of a 54:46 mixture of **10** and **11** (GLC). **10** and **11** turned out to be nonseparable on TLC analysis.

Acid-Catalyzed Reactions of 4 and 5 in Water, Methanol, and Acetic Acid. A suspension (water) or a solution (methanol and acetic acid) of the epoxide **4** or **5** (0.10 g, 0.44 mmol) in a 0.2 N solution of the acid (H_2SO_4 for the reactions in water and *p*-toluenesulfonic acid monohydrate for the reactions in methanol and acetic acid) in the solvent (10 mL) was stirred at 25 °C for 24 h (reaction in water and acetic acid) or 15 min (reaction in methanol), quenched with solid $NaHCO_3$ and saturated aqueous $NaHCO_3$ (in the case of the reaction in acetic acid the mixture was previously diluted with water), and thoroughly extracted with ether. Evaporation of the washed (water) ether extracts yielded mixtures consisting of diols **8** and **9** (reaction in water), hydroxy ethers **10** and **11** (reaction in methanol), or monoacetates (reaction in acetic acid) which were analyzed by GLC (see Tables I and II), except for the reaction carried out in acetic acid where the crude reaction obtained was analyzed by GLC only after saponification of the monoacetates to the corresponding diols **8** and **9** as described later for the reactions of **4** and **5** with trichloroacetic acid. The reaction of **4** and **5** in methanol was also performed in the presence of anhydrous $LiClO_4$ (0.5 M) to give the results reported in Table I.

The solvolysis addition products of these reactions were completely stable under the reaction conditions used.

Reaction of 4 and 5 with Methanol in CH_2Cl_2 in the Presence of *p*-Toluenesulfonic Acid. To the epoxide **4** or **5** (0.10 g, 0.44 mmol) was added a solution of *p*-toluenesulfonic acid

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monohydrate and methanol in a molar ratio (epoxide/acid/methanol) of 1:0.1:6 in anhydrous CH_2Cl_2 (10 mL) at 25 °C. The resulting mixture was stirred for 24 h at the same temperature and then treated with solid $NaHCO_3$ and saturated aqueous $NaHCO_3$. Evaporation of the washed (water) organic solvent gave a residue (0.095 g) which was analyzed by GLC (see Table I). GLC analysis of the crude product obtained by the same reaction of **4** and **5**, but stopping after different reaction times, showed the same product composition within experimental error.

Reactions of the Epoxides 4 and 5 with Trichloroacetic Acid in Several Solvents. The reactions were carried out in anhydrous benzene, cyclohexane, CCl_4, $CHCl_3$, and CH_2Cl_2 in the following way. A solution of **4** or **5** (0.10 g, 0.44 mmol) in the solvent (10 mL) at 25 °C was treated with a 1 M solution of trichloroacetic acid in the same solvent (0.48 mL), stirred for 3 h at the same temperature, washed with saturated aqueous $NaHCO_3$ and water, and evaporated to dryness. The residue obtained, consisting of mixtures of monotrichloroacetates, was hydrolyzed in the following way. The crude product was dissolved in freshly distilled THF (8 mL), treated with 1 M KOH in ethanol (2.5 mL), and then left 5 h at room temperature. Dilution with water, extraction with ether, and evaporation of the washed (water) and dried ether extracts yielded a mixture of **8** and **9** which was analyzed by GLC (see Table II). Reaction of **4** and **5** in each solvent carried out under the same conditions, but stopping after a longer reaction time of contact with the acid, yielded the same product composition within the experimental error. Experiments showed that the diols **8** and **9** are stable under the saponification conditions and that the method of saponification used does not alter the stereoselectivity of the reactions.

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Registry No. *cis*-**4**, 92695-13-1; (±)-*trans*-**5**, 92695-14-2; **6**, 1142-21-8; **7**, 1142-22-9; **8**, 63035-52-9; (±)-**9**, 92695-21-1; (±)-**10**, 92695-15-3; (±)-**11**, 92695-16-4; (±)-**12**, 92695-22-2; (±)-**19**, 92695-17-5; (±)-**20**, 92695-18-6; (±)-**21**, 92695-19-7; (±)-**22**, 92695-20-0; **24**, 63035-65-4; $PhCH_2CHO$, 122-78-1; $Ph(CH_2)_2P^+Ph_3 \cdot Br^-$, 53213-26-6; (*E*,*E*)-PhCH=CHCH=CHPh, 538-81-8.

Behavior of Benzyl Sulfoxides toward Acid Chlorides. Useful Departures from the Pummerer Reaction[1]

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The present study extends the reaction of certain electrophilic reagents with electron-rich sulfides and sulfoxides beyond previously known limits. Thus, treatment of methoxy- and, more particularly, aminobenzyl sulfoxides **2** with acyl or hydrogen chlorides gives rise in high yields to the corresponding benzyl chlorides, a departure from the normally expected Pummerer reaction. It is demonstrated that ideal substrates for this reaction are *o*-[(methylthio)methyl]anilines **1** derived from the well-known rearrangement of aromatic sulfilimines. Further, certain of the *o*-ammoniobenzyl chloride salts **4** so produced provide a basis for a novel and superior desulfurization of **1** to the corresponding *o*-methylaniline without resorting to Raney nickel.

The Pummerer reaction as generally defined[2] is the rearrangement of a sulfoxide (or sulfide at equivalent oxidation state) under acid conditions to form an α-substituted sulfide, the overall result being reduction of the sulfoxide group and oxidation of the adjacent carbon atom. Halomethyl sulfides or, via hydrolysis, aldehydes are the final products. The reaction is initiated by electrophilic attack at the sulfoxide moiety followed by expulsion of an α proton. Nucleophilic attachment at the α carbon with reduction at sulfur, results in an α-substituted sulfide.

Simple oxidative substitution of sulfides by halogen also produces α-halo sulfides.[3-5] Similarly, reactions of sulfoxides with sulfuryl chloride,[6,7] molecular chlorine,[8] and *N*-halosuccinimide[9] generally result in halogenation α to the sulfoxide.

Nevertheless, certain types of sulfides and sulfoxides have also been shown under halogenation conditions to give fission of the carbon–sulfur bond, producing an alkyl halide. References describing these studies explain such cleavage as due to a stabilizing carbonium ion intermediate. Thus, sulfides containing phthalimidomethyl,[10] benzyl-,[4b,11,12] *sec*-alkyl,[13] and *tert*-alkyl[4b] groups give the respective alkyl halide upon halogenation. In like manner, sulfoxides containing phthalimidomethyl[14] and benzyl or *tert*-butyl[15] moieties produce the respective alkyl halide along with sulfinic acid derivatives as cleavage products upon halogenation.

Less is known about such cleavage when nonoxidizing, acidic reagents are combined with sulfoxides capable of producing stabilized carbonium ion intermediates. It could be postulated, for instance, that halogen acids or acyl

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