of activation was reduced as the mole fraction of the cosolvent increased but passed through a minimum as the mole fraction of cosolvent increased further, which is analogous to TBC.[8]

Fagley and his co-workers[9] have proposed that the reorganization of the solvent at the transition state required some of the cosolvent molecules to leave the solvation shells of the ground-state substrate in order for water molecules to subsequently react with the substrate. They proposed that the unmixing of the solvent pair contributed to the measured $\Delta H^{\ddagger}$ in terms of heats of mixing or the relative partial molal enthalpies of the solvent components. Based on their model, the apparent relative partial molal enthalpy of the cosolvent, φL_2, representing an enthalpy contribution from the unmixing of all the polymeric cosolvent species that solvated the substrate, was related to the net enthalpy of activation, ΔH^*, in pure water, and observed $\Delta H^{\ddagger}$ according to eq 3, where ΔH^* is the cor-

$$\Delta H^* = \Delta H^{\ddagger} - n\varphi L_2 \quad (3)$$

rected enthalpy of activation from a binary aqueous solvent mixture to pure water, $\Delta H^{\ddagger}$ is the measured enthalpy of activation in binary solvent mixtures, φL_2 is the apparent relative partial molal enthalpy of solvent component two (acetone or ethanol), and n is the number of cosolvent molecules leaving the solvation shell at the transition state as an n-mer. The above correlations were examined in Table II for both CEES and CEMS using published data on the relative partial molal enthalpies of the solvent systems.[20,21] The corrected ΔH^* for CEES hydrolysis in pure water from acetone–water was very close to that from ethanol–water mixtures at 19.4 ± 0.8 kcal/mol. This was also consistent with $\Delta H^{\ddagger}$ = 19.5 kcal/mol at 25 °C determined from the extrapolated k values of 5.01×10^{-3} and 4.90×10^{-2} s^{-1} at 15 and 35 °C, respectively, for pure water. The corrected $\Delta H^{\ddagger}$ for CEMS hydrolysis was 19.3 ± 0.03 kcal/mol, consistent with the 19.7 ± 0.05 kcal/mol value reported by Blandamer et al.[4]

The entropies of activation were calculated from k and $\Delta H^{\ddagger}$ at 25 °C and listed in Table 3 (supplementary material). They decreased as the mole fraction of the cosolvent increased and were lower than that of TBC when compared in the same solvent systems. This may suggest that the formation of the three-membered ring structure of the sulfonium ion was less favored than the carbonium ion and that the decrease in $\Delta S^{\ddagger}$ in the presence of the cosolvent was caused by an increase in the water structure of the aqueous system. This made the ground-state solvation shells more difficult to break, resulting in a decrease in both entropy of activation and k relative to that in pure water.

Registry No. CEES, 693-07-2; CEMS, 542-81-4; TBC, 507-20-0.

Supplementary Material Available: Tables 3–8 depicting rate coefficients for hydrolysis and results of analysis for heat capacities of activation (6 pages). Ordering information is given on any current masthead.

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Ring-Opening Reactions of *cis*- and *trans*-2,3-Bis(4-methoxybenzyl)oxirane: Competition between Assistance by and Migration of an Aryl Group

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Received December 17, 1985

The study of the aryl participation in the oxirane ring-opening reactions in acidic conditions was extended to (*p*-methoxybenzyl)oxiranes *cis*-**2b** and *trans*-**3b** analogous to the ones unsubstituted on the phenyl ring, **2a** and **3a**, previously studied. The introduction of the *p*-methoxy group causes in the trans epoxide **3** the appearance of the syn adduct in the methanolysis reactions and a large increase in the same adduct in the hydrolysis, acetolysis, and trichloroacetolysis reactions. For the cis epoxide **2**, the presence of the para substituent causes the loss of complete anti stereoselectivity: in all the reactions but acetolysis, significant amounts of syn adduct are formed. Furthermore some reactions (see methanolysis) of the *p*-methoxy-substituted compounds **2b** and **3b** reveal the presence of significant amounts of rearranged 1,3-addition products of the type **31** and **29**, respectively, contrary to the corresponding reactions of the epoxides **2a** and **3a**. Except for the trichloroacetolysis in CH_2Cl_2, all the reactions of the trans epoxide **3b** show a higher syn stereoselectivity than do the corresponding reactions of the cis epoxide **2b**. The results obtained for the reactions of *p*-methoxy-substituted epoxides **2b** and **3b** further confirm the mechanism previously proposed in order to rationalize the reactions of the unsubstituted epoxides **2a** and **3a**, which involves the neighboring participation of the phenyl. However the presence of rearranged 1,3-addition compounds among the reaction products led us to insert into the mechanistic scheme the necessary modifications which imply competition between assistance by and migration of the aryl group.

The reactions under acidic conditions of oxiranes bearing neither aryl nor any other unsaturated system directly linked to the heterocyclic ring usually occur with complete or near complete anti stereoselectivity.[1-3] However, when either aryls, double bonds, or other unsaturated systems are directly linked to the oxirane ring, the steric course of the ring opening can range from complete retention to complete inversion of its configuration depending on the structure of the epoxide and on the reaction condition used.[1,2,4,5] In the case of 2-aryloxiranes the amounts of

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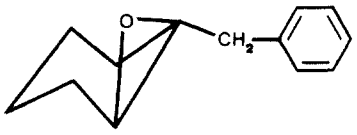
0022-3263/86/1951-2759$01.50/0

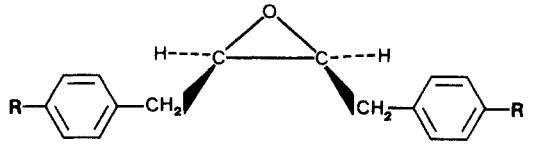
the syn adducts were found to be strictly related to the capability of the aromatic moiety to stabilize the benzylic carbocationic structures formed.[4,5]

As a part of a research program aimed at controlling the selectivity in the ring opening of 1,2-epoxides bearing "particular substituents" on the ring,[5-7] we considered 2-benzyloxiranes[8] in which the insertion of a methylene group between the aromatic portion and the oxirane carbon does not allow any mesomeric interaction between the aryl and carbocationic center formed in the acid-catalyzed ring-opening process. The presence of substantial amounts of syn adducts in the acid-catalyzed ring-opening reactions of 1-benzylcyclohexene oxide (1)[8] lead us to point out, for the first time, the capability of a phenyl, not directly linked to an oxirane ring, to participate in the epoxide ring-opening process. The reactions of epoxide **1** were ra-



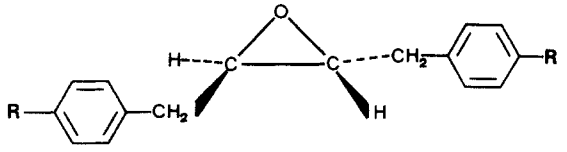
1

tionalized[8] on the basis of a competition between the pathway, usual for simple alkyl-substituted epoxides, leading to the anti adducts and the other one, implying the formation of phenonium type intermediates, leading to the syn adducts. In order to define better the neighboring participation by a phenyl in the ring opening process of oxiranes, we initially extended our studies to the *cis*- and *trans*-2,3-dibenzyloxirane (**2a**,**3a**)[9] in which the equivalence of the two oxirane carbons should facilitate the stereochemical study of the ring opening and consequently the study of the aryl participation in these systems. The study of the reactions of these epoxides (**2a** and **3a**) demonstrates a clear dependence of the participation of the phenyl, in the oxirane ring-opening process, on the configuration of the epoxide.[9] Whereas the reactions of the cis epoxide **2a** exhibit no participation, the ring-opening process of the trans isomer **3a** occurs, at least in part, through a nucleophilic participation of the phenyl.[9] The results were rationalized, also in this case, through a mechanism (schematized for clarity only for the trans epoxide **3a**; see Scheme IV) which implies a competition between the aryl-unassisted and the aryl-assisted pathway.[9] According to this scheme[9] the direct attack of the nucleophile on the intramolecular intimate ion-dipole pair **25** (arising from the protonated epoxide **24**) affords the anti adducts **28**. On the other hand, neighboring aryl participation at the β-former oxirane carbon of the same species (**25**) yields the phenonium-type ion **26**. The attack of the nucleophile from the side opposite the phenonium bridge of **26** yields the syn adducts **27**. The lack of participation in the cis epoxide **2a** was assumed to be due to the severe steric interactions that arise in the formation of the corresponding phenonium-type species **30**.[9] No traces were found, in the reactions of either the epoxide **2a** or **3a**, of the 1,3-rearranged addition products of type **31** (from **2a**) and **29** (from **3a**). The rearranged compounds **31** and **29** could have been formed by the attack of the nucleophile on the less substituted carbon of the intermediate phenonium ions **30** and **26**, respectively. This kind of rearrangement of an aryl from the less substituted carbon to the more substituted one is quite unusual in aryl-assisted solvolysis of simple substrates.[10,11] However, compounds **31** and **29** could be expected on the basis of the results obtained by Dubois in aryl-assisted reactions in which the phenonium ion type intermediate possesses an electron-withdrawing substituent in the vicinity of the more substituted carbon.[11]



2a, R = H

2b, R = OCH_3



3a, R = H

3b, R = OCH_3

Our research was successively extended to epoxides of type **2a** and **3a** substituted on the phenyl, namely, the *p*-methoxy-substituted epoxides **2b** and **3b**, in order to evaluate better the limits and the degree of the aryl participation in a Hammett sense. The inductive and the conjugative effects of the *p*-methoxy group should have modified in some way the course of the ring-opening reactions of the oxirane ring in these systems.

Results

Cis epoxide **2b** and trans epoxide **3b** and pure reference primary 1,2-addition products [diols **4b** and **5b** (hydrolysis reactions) and 1,2-methoxy alcohols **6b** and **7b**] and secondary rearranged 1,3-addition products of type **31** and **29** [1,3-diols **8b** and **9b** (hydrolysis reactions), and 1,3-methoxy alcohols **10b** and **11b** (methanolysis reactions)] were prepared in the following manner (see Schemes I, II, and III). The Wittig reaction of (*p*-methoxyphenyl)-acetaldehyde (**12**) with the ylide derived from 2-(*p*-methoxyphenyl)ethyltriphenylphosphonium bromide (**13**)[12] yielded a 89:11 mixture of the *cis*-olefin **14b** and *trans*-olefin **15b**, contrary to the previous report[12] in which only the cis isomer (**14b**) was detected. Equilibration of the 89:11 mixture of **14b** and **15b** by photochemical irradiation yielded a 48:52 mixture of the same compounds. Column chromatography of the mixtures of the *cis*-olefin **14b** and *trans*-olefin **15b** on 15% $AgNO_3/SiO_2$ afforded the pure

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Table I. Product Composition in the Ring-Opening Reactions of Epoxides *cis*-2a,b and *trans*-3a,b in Acidic Methanol

			2			3		
para substituent[a]	reagents		syn adduct[b]	anti adduct[c]	rearranged adduct[d]	syn adduct[c]	anti adduct[b]	rearranged adduct[e]
a	MeOH	H_2SO_4	0[f]	100[f]	0[f,g]	0[f]	100[f]	0[f,g]
b	MeOH	H_2SO_4	2.6	97.4	0	35.8	50.8	13.4
a	MeOH–$LiClO_4$[h]	TsOH	0[f]	100[f]	0[f,g]	0[f]	100[f]	0[f,g]
b	MeOH–$LiClO_4$[h]	TsOH	3.9	89.8	6.3	38.3	38.0	23.7

[a] **a**, *p*-H derivatives; **b**, *p*-OCH_3 derivatives. [b] Pref methoxy alcohol **6**. [c] Parf methoxy alcohol **7**. [d] 1,3-Methoxy alcohol **10**. [e] 1,3-methoxy alcohol **11**. [f] Reference 9. [g] Reference 19. [h] 0.5 M solution in $LiClO_4$.

Table II. Product Composition in the Hydrolysis, Trichloroacetolysis, and Acetolysis of Epoxides *cis*-2a,b and *trans*-3a,b

			2		3	
para substituent[a]	reagents		syn adduct[b]	anti adduct[c]	syn adduct[c]	anti adduct[b]
a	H_2O	H_2SO_4	0[d]	100[d]	11.5[d]	88.5[d]
b	H_2O	H_2SO_4	17.5	82.5	65.8	34.2
a	cyclohexane	CCl_3COOH[e]	0[d]	100[d]	2.2[d]	97.8[d]
b	cyclohexane	CCl_3COOH[e]	27.8	72.2	78.0	22.0
a	CCl_4	CCl_3COOH[e]	0[d]	100[d]	3.0[d]	97.0[d]
b	CCl_4	CCl_4COOH[e]	34.0	66.0	82.0	18.0
a	benzene	CCl_3COOH[e]	0[d]	100[d]	8.4[d]	91.6[d]
b	benzene	CCl_3COOH[e]	43.5	56.5	88.0	12.0
a	$CHCl_3$	CCl_3COOH[e]	0[d]	100[d]	8.6[d]	91.4[d]
b	$CHCl_3$	CCl_3COOH[e]	65.7	34.3	93.0	7.0
a	CH_2Cl_2	CCl_3COOH[e]	0[d]	100[d]	21.7[d]	78.3[d]
b	CH_2Cl_2	CCl_3COOH[e]	100	0	96.0	4.0
a	CH_3COOH	TsOH[e]	0[d]	100[d]	5.0[d]	95.0[d]
b	CH_3COOH	TsOH[e]	0	100	92.0	8.0

[a] **a**, *p*-H derivatives; **b**, *p*-OCH_3 derivatives. [b] *meso* diol **4**. [c] *d,l* diol **5**. [d] Reference 9. [e] After saponification of the crude reaction mixture.

compounds. The (*p*-methoxyphenyl)acetaldehyde (**12**)[12,13] cannot be easily obtained by direct oxidation of the corresponding alcohol with various agents.[14] However aldehyde **12** was obtained in a very convenient way through the Darzenz condensation[15] of *p*-anisaldehyde (**16**) with methyl α-chloroacetate (**17**) followed by the thermal decarboxylation of the glycidic acid **19** formed by saponification of the ester **18**. Direct epoxidation of the *cis*-olefin **14b** and *trans*-olefin **15b** with *m*-chloroperoxybenzoic acid (MCPBA) yielded the corresponding epoxides **2b** and **3b**. The *meso* diol **4b** and the *d,l* diol **5b** were prepared by stereospecific cis dihydroxylation of the *cis*-olefin **14b** and *trans*-olefin **15b** with OsO_4.[16] The pref[17] methoxy alcohol **6b** and the parf[17] methoxy alcohol **7b** were stereospecifically obtained by base-catalyzed methanolysis of the trans epoxide **3b** and cis epoxide **2b**. The ring opening of oxiranes under strongly basic conditions is known to occur through a S_N2-type substitution with complete inversion of the configuration.[1,2,4d,18] The rearranged 1,3-derivatives **8b** and **9b** and **10b** and **11b** were obtained according to a synthetic scheme (see Scheme III) analogous to the one previously followed for the synthesis of the corresponding derivatives unsubstituted on the phenyl.[19] The $NaBH_4$–EtOH reduction of the β-keto ester **21b**, obtained by Claisen-type condensation of ethyl (*p*-methoxyphenyl)acetate (**20b**), yielded a 69:31 mixture of diastereoisomer hydroxy esters pref[17] **22b** and parf[17] **23b** which were separated and converted by LAH reduction to the corresponding 1,3-diols pref[17] **8b** and parf[17] **9b**. The diols **8b** and **9b** were transformed into their primary methoxy derivatives, pref[17] **10b** and parf[17] **11b**, respectively, by controlled methylation with a CH_3I–NaH system.

The structures and configurations of the olefins **14b** and **15b**, of the epoxides **2b** and **3b**, of the 1,2-diols **4b** and **5b**, and of the 1,2-methoxy alcohols **6b** and **7b**, were inferred on the basis of their ^1H NMR spectra through direct comparison with the spectra of the corresponding compounds having no substituents on the phenyl ring (**14a**, **15a**, **2a–7a**).[9] Apart from the signal of the methoxy group present in the methoxy-substituted **b** series and from a different pattern of the signal of the aromatic protons, the spectra of each couple of compounds (**a** and **b**) are practically superimposable. Also the structures and configurations of the 1,3-diols **8b** and **9b**, of the 1,3-methoxy alcohols **10b** and **11b**, and of the hydroxy esters **22b** and **23b** became evident by a comparison of their ^1H NMR spectra with the spectra of the corresponding derivatives without substituents on the phenyls (**8a**, **9a**; **10a**, **11a**; **22a**, **23a**)[19] whose structure and configuration had been firmly established. As in the case of the 1,2-derivatives, here too a close analogy was found in the spectra of the **a** and **b** series.

The results of the acid-catalyzed methanolysis, hydrolysis, acetolysis, and trichloroacetolysis of epoxides **2b** and **3b** under different conditions are summarized in Tables I and II; the corresponding data for the unsubstituted epoxides **2a** and **3a**[9] are reported in the same tables for the sake of comparison. Whereas the methanolysis and hydrolysis reactions were directly analyzed by GLC, the reaction mixtures of the acetolysis and trichloroacetolysis were examined only after saponification of the monoesters obtained.

Discussion

An inspection of the results obtained reveals marked and interesting differences between the reactions of the *p*-methoxy-substituted epoxides **2b** and **3b** and the corresponding ones of the epoxides without substituent on the aryl groups (**2a** and **3a**). In particular the introduction of the *p*-methoxy groups causes, in the trans epoxide **3**, the

(13) Karabastos, G. J.; Bushman, D. W. *Tetrahedron* **1975**, *31*, 1471.
(14) Crotti, P.; Macchia, F. *J. Org. Chem.* **1983**, *48*, 1350.
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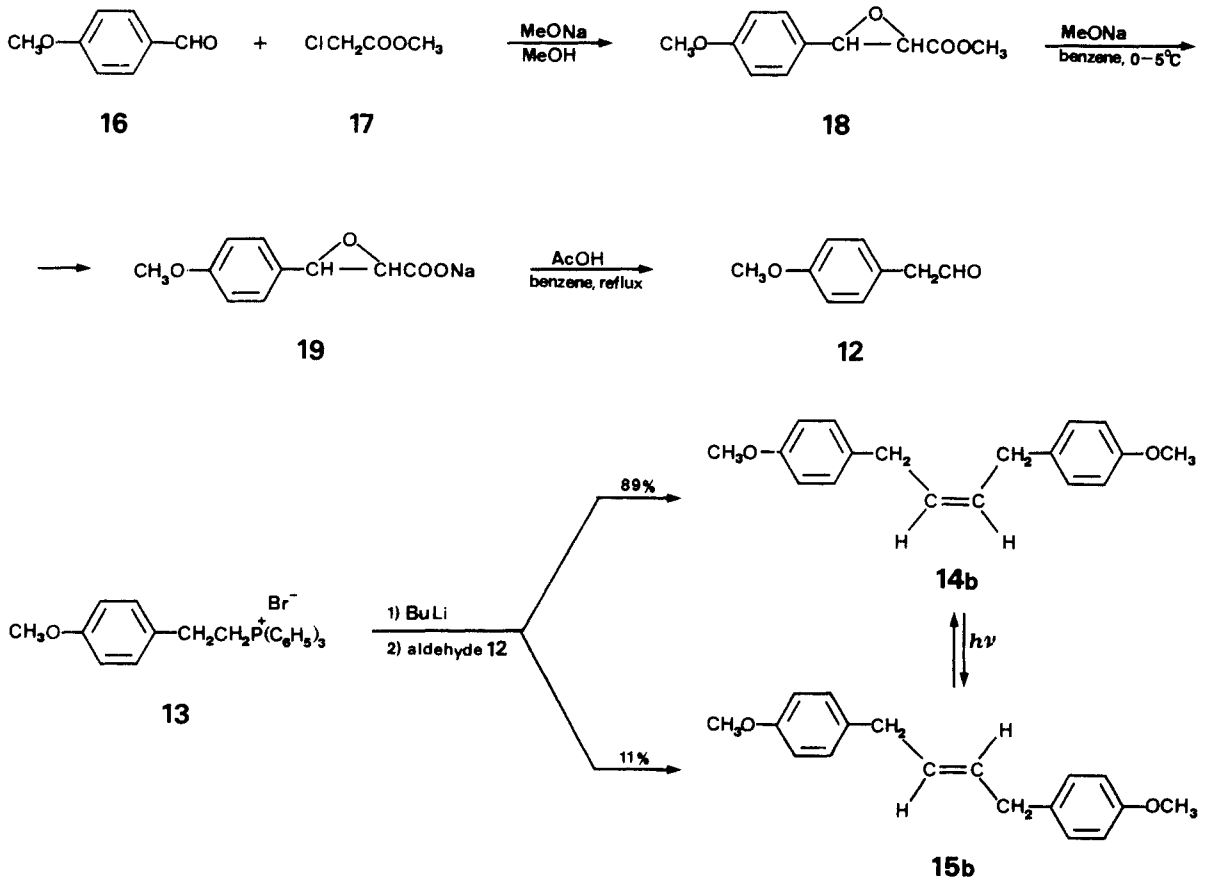
(17) The proposal of F. A. Carey and M. E. Kuehne for specifying relative configuration in molecules with multiple chiral centres has been adopted in order to avoid the ambiguous descriptors erythro and threo see: Carey, F. A.; Kuehne, M. E. *J. Org. Chem.* **1982**, *47*, 3812.
(18) Brewster, J. H. *J. Am. Chem. Soc.* **1956**, *78*, 4061.
(19) Crotti, P.; Macchia, F.; Stoppioni, A. *Gazz. Chim. Ital.* **1985**, *115*, 269.

Scheme I

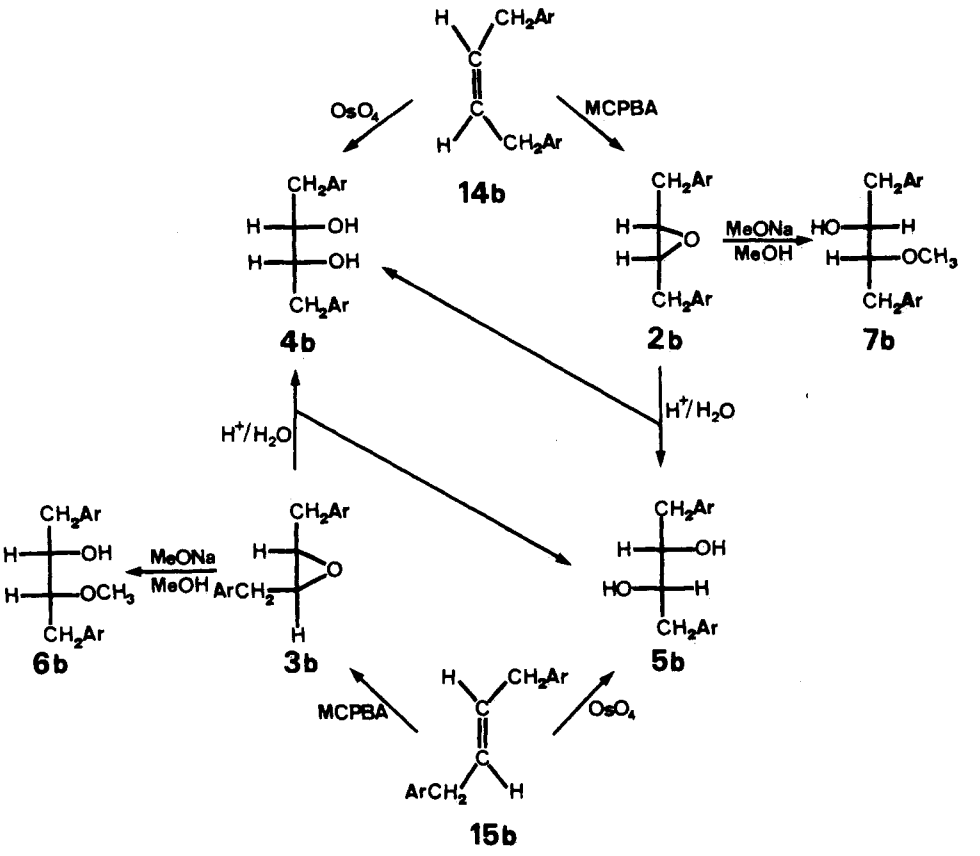


appearance of the syn adduct in the methanolysis reactions (see Table I) and a large increase in the same adduct in the hydrolysis, acetolysis, and trichloroacetolysis reactions (see Table II). As for the cis epoxide **2** the presence of the *p*-methoxy substituent causes the loss of complete anti stereoselectivity: in all the reactions but acetolysis, significant amounts of syn adduct are formed. Furthermore, some reactions (see methanolyses) of the *p*-methoxy-substituted compounds **2b** and **3b** reveal the presence of significant amounts of rearranged 1,3-addition products of type **31** and **29**, respectively, contrary to the corresponding reaction of the unsubstituted epoxides.[9] Except for the trichloroacetolysis in CH_2Cl_2, all the reactions of the trans epoxide **3b** show higher syn stereoselectivity (that is a higher syn/anti product ratio) than do the corresponding reactions of the cis epoxide **2b**, confirming the analogous trend observed for the reactions of the unsubstituted epoxides.[9] Finally a marked increase in the syn stereoselectivity of the trichloroacetolysis of both the cis epoxide **2b** and trans epoxide **3b** with the polarity of the nonprotic medium is observed.

The results obtained for the reactions of the *p*-methoxy-substituted epoxides **2b** and **3b** and in particular the formation of rearranged 1,3-addition products of type **31** and **29** further confirm the mechanism, previously proposed in order to rationalize the reactions of the unsubstituted epoxides **2a** and **3a**, which implies neighboring participation of the aryl.[9] However, the presence of compounds of type **29** and **31** among the reaction products led us to insert into the mechanistic scheme the necessary modifications (see Scheme IV) that imply competition between assistance by and migration of the aryl group. The modified scheme now involves the further possibility of the attack of the nucleophile on the less substituted carbon of the phenonium ion intermediates **26** or **30** affording the rearranged 1,3-adducts **29** or **31**, respectively. As for the trans epoxides **3** the strong mesomeric electron-releasing effect of the *p*-methoxy group markedly increases the nucleophilic character of the aryl, thus directing the course of the reaction along the aryl-assisted pathway. In the case of the cis epoxide **2b** the same effect is able to give rise to substantial aryl participation which is lacking in the unsubstituted epoxide **2a**.[9] However, the highly unfavorable steric interactions, which arise during the formation of the phenonium ion species of type **30**[9] from cis epoxide **2**, make the aryl participation still lower in **2b** than in the trans isomer **3b**. The formation of the rearranged 1,3-addition products of type **31** and **29** in the methanolyses of the *p*-methoxy-substituted epoxides **2b** and **3b** agrees with the expectations based on the results obtained by Dubois.[11] Evidently the presence of an electron-withdrawing group (the OH group) in the vicinity of the more substituted carbon of the phenonium ion intermediates **26** or **30** is able, also in the present case, to make the attack of the nucleotphile on that carbon no longer exclusive, thus clearing the pathway leading to the rearranged products **29** or **31**. However, it is not easy to understand why in all the other reactions but the methanolyses of the epoxide **2b** and **3b** the rearranged products **31b** or **29b** are not formed at all, in spite of the substantial contribution, in these reactions of the pathways implying the formation of phenonium ion species **30** or **26**, as it is demonstrated by the formation of large amounts of syn 1,2-adducts (see Table II). As for the rearranged products **31b** and **29b** formed in the methanolyses of **2b** and **3b**, it is also worthwhile noting that the addition of a salt ($LiClO_4$), which increases the polarity of the medium, leads to a net increase in their amounts.

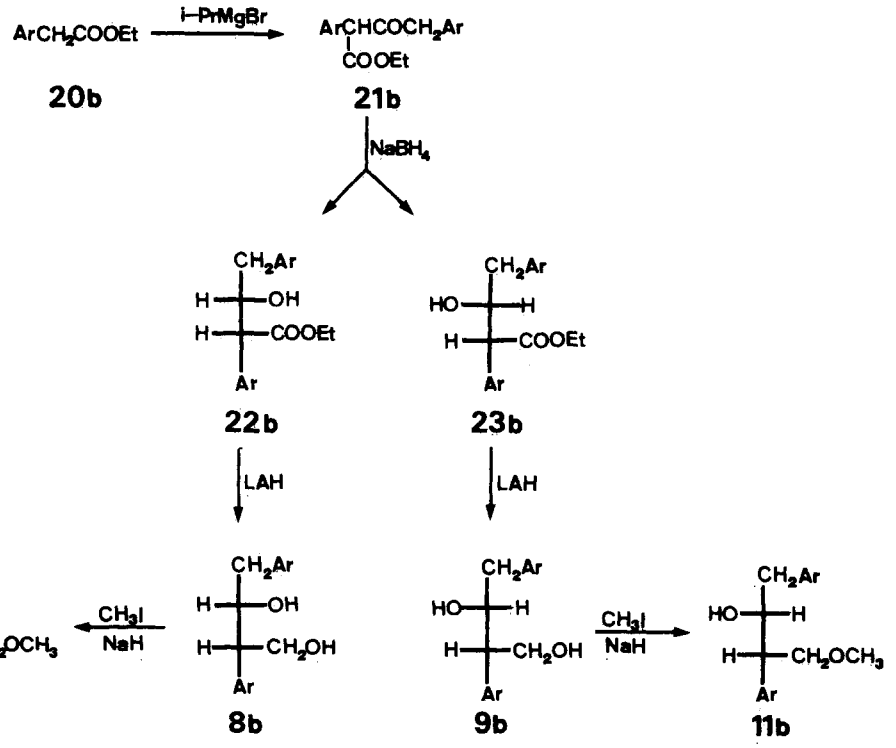
As previously underlined in the case of the reactions of 1-benzylcyclohexene 1,2-epoxide (**1**)[8] and in the case of the

Scheme II



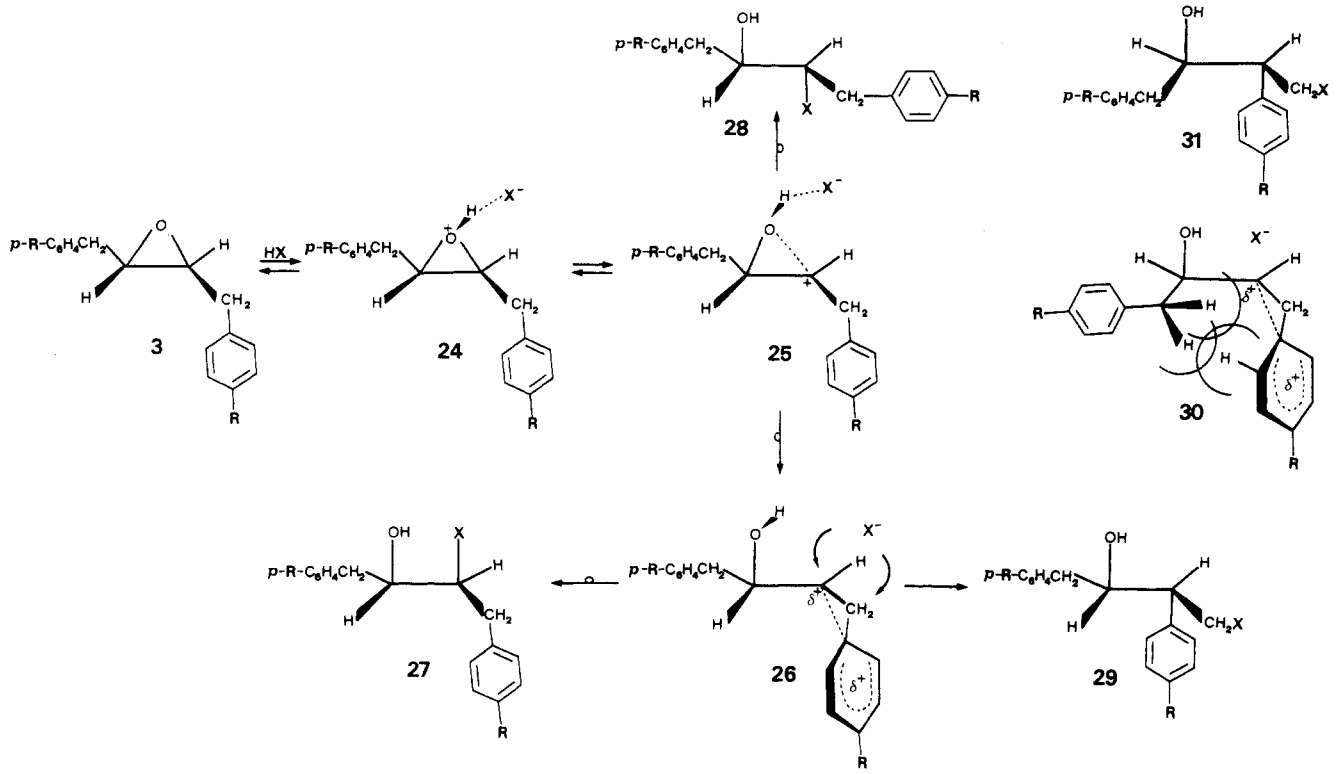
Ar= p-$CH_3OC_6H_4$

Scheme III



Ar= p-$CH_3OC_6H_4$

Scheme IV



a, R = H
b, R = OCH_3

unsubstituted 2,3-dibenzyloxiranes (**2a** and **3a**),[9] the reactions of the *p*-methoxy-substituted derivatives **2b** and **3b** also exhibit large differences in stereoselectivity and therefore in aryl participation, depending on the reaction conditions. In particular the trichloroacetolysis reactions of both the trans epoxide **3a** and the cis epoxide **2b** lead to high percentages of syn adduct which markedly increase, for both the epoxides, in the following solvent series: cyclohexane, CCl_4, benzene, $CHCl_3$, CH_2Cl_2; the syn/anti ratio passes from 27.8:72.2 to 100:0 for epoxide **2b** and from 78.0:22.0 to 96.0:4.0 for epoxide **3b**. An analogous solvent-dependent stereoselectivity has been observed in the trichloroacetolysis of 1-aryl-[4c] and 1-ethynylcyclohexene epoxides.[5] However, as the mechanism proposed[4c,5] at that time for those substrates do not fit with the present results, a complete rationalization of this strong solvent effect still remains to be worked out.[8,9]

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 mixtures of diols **4b** and **5b**, of hydroxy ethers **6b**, **7b**, and **10b** (from cis epoxide **2b**) and **6b**, **7b**, and **11b** (from trans epoxide **3b**), and of olefins **14b** and **15b** were run on a Dani Gas Cromatograph 3800 apparatus with a flame ionization detector with SE 52 capillary glass column (20 m × 0.2 mm; column, 240 °C, evaporator and detector, 270 °C; nitrogen flow, 2 mL/min; due to the overlapping of the peaks of the hydroxy ethers **6b** and **10b**, the methanolysis crude reaction mixtures from epoxide **2b** were analyzed only after transformation of the obtained hydroxy ethers into their trimethylsilyl derivatives); the order of increasing retention times was **5b** < **4b**; **10b** < **7b** < **6b** (trimethylsilyl derivatives); **7b** < **11b** < **6b**; **15b** < **14b**. Also mixtures of hydroxy esters **22b** and **23b** were GLC determined on the same apparatus in the following conditions: column, 210 °C; evaporator and detector, 250 °C; nitrogen flow, 2 mL/min; the order of increasing retention times was **22b** < **23b**. TLC was performed on 2 mm layer silica gel plates (Merck F_{254}) containing a fluorescent indicator. All comparison 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 with bp 40–70 °C. Evaporations were made 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.

Methyl 3-(4-Methoxyphenyl)glycidate (18). A solution of 4-methoxybenzaldehyde (48.9 g, 0.36 mol) and methyl chloroacetate (58 g, 0.54 mol) was added to a solution of CH_3ONa (from 12.4 g of Na, 0.54 g atom) in anhydrous CH_3OH (180 mL), with the temperature kept at −10 °C. After the addition was completed, the mixture was stirred at −5 °C for 2 h and then for 3 h at room temperature. The mixture was poured into ice–water (700 mL) containing AcOH (4 mL); the precipitated white solid was filtered, washed (water), and dried in a desiccator, affording crude **18** (85 g), which was pure enough for next reaction: NMR δ 4.10 and 3.56 (2 d, 1 each, J = 2.0 Hz, $\overline{CHCHO}$), 3.87 (s, 6, $CH_3OC_6H_4$ and $COOCH_3$). A sample of **18** was recrystallized from MeOH to give pure **18**, mp 69–70 °C. Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.20; H, 5.75.

Sodium Salt of 3-(4-Methoxyphenyl)glycidic Acid (19). A solution of CH_3ONa (from 7.4 g of Na, 0.32 mol) in anhydrous methanol (110 mL) was slowly added to a stirred solution of **18** (65 g, 0.31 mol) in anhydrous benzene (480 mL); the reaction temperature was maintained between 0 and 5 °C. Water (7.5 mL) was then added in one portion, and the reaction mixture was left at 5–10 °C for 2 h. Filtering and washing (Et_2O) of the precipitated solid afforded crude **19** (52 g), which was directly used for the next reaction.

(4-Methoxyphenyl)acetaldehyde (12). A stirred suspension of **19** (20 g, 0.092 mol) was treated with AcOH (5.2 mL, 0.092 mol), and the reaction mixture was gently refluxed for 3 h. After the mixture was cooled, the organic layer was separated, washed (water, saturated aqueous $NaHCO_3$ solution), dried and evapo-

rated to give **12** practically pure.

***cis*- and *trans*-1,4-Bis(4-methoxyphenyl)-2-butene (14b and 15b).** Wittig reaction between aldehyde **12** (7.0 g, 46.6 mmol) and the ylide derived from 2-(4-methoxyphenyl)ethyltriphenylphosphonium bromide (28.0 g, 58.7 mmol) by butyllithium (36.68 mL of a 1.6 M solution), as previously described,[12] afforded a crude reaction product (15.5 g) mostly consisting of a 89:11 mixture of **14b** and **15b** (GLC). Extraction with warm petroleum ether of the crude reaction mixture and successive evaporation of the organic solvent afforded a semisolid residue (8.5 g), which was filtered on a short silica gel column by eluting with a 95:5 mixture of petroleum ether and ether, from which 80-mL fractions were collected. The second and third fractions yielded a solid (5.2 g) consisting of a mixture of **14b** and **15b** in the ratio 87:13 (GLC).

The above 87:13 mixture of **14b** and **15b** (5.1 g) in EtOH (200 mL) was irradiated with the full intensity of a 70-W high-pressure mercury lamp (Hanau, Model TQ 81), equipped with an immersion well system. After 48 h of irradiation, the **14b–15b** ratio turned out to be 48:52 (GLC); this ratio did not change significantly with increasing the irradiation time. Evaporation of the ethanolic solution afforded a crude solid product, which was chromatographed through a 15% $AgNO_3/SiO_2$(200 g) column, from which 50-mL fractions were collected. Elution was carried out, successively, with 93:7 (1.0 L), 90:10 (500 mL), 85:15 (600 mL), 80:20 (500 mL), 75:25 (500 mL), 70:30 (2.5 L), 50:50 (500 mL), and 30:70 (500 mL) petroleum ether–ether mixtures and finally with ether (2.0 L). The fractions 47–80 were combined to give pure **15b** (1.1 g), as a solid, mp 65–66 °C: NMR δ 5.56 (m, 2, CH=CH), 3.76 (s, 6, 2 CH_3O), 3.25 (d, 4, J = 5.0 Hz, 2 $ArCH_2$). Anal. Calcd for $C_{18}H_{20}O_2$: C, 80, 56; H, 7.51. Found: C, 80.25; H, 7.34.

The fractions 132–167 yielded pure **14b** (2.56 g) as a solid, mp 36–37 °C [lit.[12] bp 128–131 °C (0.15 mm)].

***cis*-2,3-Bis(4-methoxybenzyl)oxirane (2b).** A cooled solution (−15 °C) of **14b** (2.32 g, 8.6 mmol) in $CHCl_3$ (90 mL) was treated portionwise under stirring with 90% MCPBA (1.65 g, 8.6 mmol). After the addition was completed, the reaction mixture was stirred for 1 h at −15 °C and then left 24 h at 5 °C. Evaporation of the washed (saturated aqueous $NaHCO_3$ and water) and dried organic solution yielded a solid residue (2.30 g) consisting of **2b**, which on recrystallization from petroleum ether afforded pure **2b** (1.57 g), mp 56.5–57.5 °C: NMR δ 3.83 (s, 6, 2 CH_3O), 3.23 (m, 2, CHCHO), 3.00 (m, 4, 2 $ArCH_2$). Anal. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 76.18; H, 7.25.

***trans*-2,3-Bis(4-methoxybenzyl)oxirane (3b).** Analogous treatment of *trans*-olefin **15b** (0.76 g, 2.82 mmol) in $CHCl_3$ (40 mL) with 90% MCPBA (0.542 g, 2.82 mmol) afforded a crude solid product (0.75 g), which was recrystallized from petroleum ether to give pure **3b** (0.35 g), mp 61–62 °C; NMR δ 3.80 (s, 6, 2 CH_3O), 2.84 (m, 6, 2 $ArCH_2CH$). Anal. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 75.80; H, 7.15.

***meso*-1,4-Bis(4-methoxyphenyl)-2,3-butanediol (4b).** Treatment of olefin **14b** (0.68 g, 2.5 mmol) with OsO_4 (0.010 g) in the presence of *N*-methylmorpholine *N*-oxide hydrate (0.39 g, 2.6 mmol) as previously described[9] afforded a solid residue (0.090 g), which on recrystallization from petroleum ether (bp 100–140 °C) afforded pure **4b** (0.040 g), mp 162–163 °C: IR λ 2.98 μm (OH); NMR δ 3.46 (s, 6, 2 CH_3O) [this signal overlaps the multiplet corresponding to the two protons HOCHCHOH], 2.76 (m, 4, 2 $ArCH_2$). Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.30; H, 7.10.

***d,l*-1,4-Bis(4-methoxyphenyl)-2,3-butanediol (5b).** Analogous treatment of *trans*-olefin **15b** (0.53 g, 2 mmol) afforded pure **5b** (0.020 g) after recrystallization from petroleum ether (bp 100–140 °C) of the crude reaction product: mp 132–134 °C; IR λ 3.00 μm (OH); NMR δ 3.77 (s, 6, 2 CH_3O) [this signal overlaps the multiplet corresponding to the two protons HOCHCHOH], 2.77 (m, 4, 2 $ArCH_2$). Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.65; H, 7.30.

Reaction of Epoxide 2b with Trichloroacetic Acid in Anhydrous CH_2Cl_2. A solution of epoxide **2b** (0.20 g, 0.70 mmol) in anhydrous CH_2Cl_2 (20 mL) was treated with 1 N CCl_3COOH solution in anhydrous CH_2Cl_2 (0.77 mL), and the resulting reaction mixture was left 5 days at room temperature. Evaporation of the washed (saturated aqueous $NaHCO_3$ and water) and dried organic solution afforded a liquid residue (0.22 g), which was dissolved in anhydrous ether (20 mL) and treated with LAH (0.20 g). The reaction mixture was stirred 30 min at room temperature, and then water and 10% aqueous NaOH solution were added in order to destroy the excess of hydride. Evaporation of the dried ether solution afforded a solid residue (0.19 g), which was recrystallized from petroleum ether (bp 100–140 °C) to give pure **4b** (0.060 g).

Reaction of Epoxide 3b with Trichloroacetic Acid in Anhydrous CH_2Cl_2. A solution of epoxide **3b** (0.10 g, 0.35 mmol) in anhydrous CH_2Cl_2 (10 mL) was treated with 1 N CCl_3COOH in the same solvent (0.38 mL) as described above for the corresponding reaction of epoxide **2b**, to give, after LAH reduction, a crude reaction product (0.090 g), which on recrystallization from petroleum ether (bp 100–140 °C) afforded pure **5b** (0.025 g).

Reaction of Epoxide 2b with 0.2 N H_2SO_4. A suspension of epoxide **2b** (0.070 g) in 0.2 N H_2SO_4 (7 mL) was stirred at 50–60 °C for 3 days. After the mixture was cooled, 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 (0.070 g), which on recrystallization from petroleum ether (bp 100–140 °C) gave pure diol **5b** (0.035 g).

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

***parf*-3-Methoxy-1,4-bis(4-methoxyphenyl)-2-butanol (7b).** Cis epoxide **2b** (0.10 g) in anhydrous methanol (5 mL) was added to a stirred solution of CH_3ONa (from 1.0 g of Na) in anhydrous methanol (20 mL); the resulting mixture was refluxed for 6 h, then cooled, diluted with water, and extracted with ether. Evaporation of the washed (water) and dried ether extracts yielded a liquid residue (0.10 g), consisting of hydroxy ether **7b**, which was subjected to semipreparative TLC on 0.5-mm silica gel plates (a 50:50 mixture of petroleum ether and ether was used as the eluent; elution was repeated three times). Extraction of the most intense band (R_f 0.50) afforded pure **7b** (0.060 g) (GLC) as a liquid: IR λ 2.93 μm (OH); NMR δ 4.50 (m, 1, $CHOCH_3$), 3.83 (s, 6, 2 $ArOCH_3$), 3.66 (m, 1, CHOH), 3.37 (s, 3, $CHOCH_3$), 2.83 (m, 4, 2 $ArCH_2$). Anal. Calcd for $C_{19}H_{24}O_4$: C, 72.12; H, 7.65. Found: C, 72.40; H, 7.75.

***pref*-3-Methoxy-1,4-bis(4-methoxyphenyl)-2-butanol (6b).** Analogous treatment of trans epoxide **3b** (0.10 g), as described above for **7b**, afforded a liquid residue (0.090 g) consisting of hydroxy ether **6b**, which was purified by semipreparative TLC on 0.5-mm silica gel plates (a 50:50 mixture of petroleum ether and ether was used as the eluent; elution was repeated three times). Extraction of the most intense band (R_f 0.48) afforded pure **6b** (0.050 g) (GLC) as a liquid: IR λ 2.92 μm (OH); NMR δ 4.33 (m, 1, $CHOCH_3$), 3.80 (s, 6, 2 $ArOCH_3$) [this last signal overlaps completely the multiplet corresponding to the signal of the methine proton (CHOH)]; 3.30 (s, 3, $CHOCH_3$), 2.87 (m, 4, 2 $ArCH_2$). Anal. Calcd for $C_{19}H_{24}O_4$: C, 72.12; H, 7.65. Found: C, 72.35; H, 7.75.

Reaction of Epoxide 2b with 0.2 N H_2SO_4 in Anhydrous Methanol. Epoxide **2b** (0.090 g) in 0.2 N H_2SO_4 solution in anhydrous methanol (9 mL) was left at room temperature for 24 h. Water was added and the suspension extracted with ether; evaporation of the washed (saturated aqueous $NaHCO_3$ and water) and dried ether extracts afforded a crude reaction product (0.085 g), which was subjected to semipreparative TLC on 0.5-mm silica gel plate (a 50:50 mixture of petroleum ether and ether was used as the eluent; elution was repeated three times). Extraction of the most intense band afforded pure **7b** (0.050 g).

Ethyl 3-Oxo-2,4-bis(4-methoxyphenyl)butanoate (21b). Ethyl (4-methoxyphenyl)acetate (11.6 g, 0.06 mol) was slowly added to a stirred solution of isopropylmagnesium bromide from Mg (2.4 g, 0.1 mol) and isopropyl bromide (12.3 g, 0.1 mol) in anhydrous ether (20 mL). After being stirred for 1 h at room temperature, the reaction mixture was hydrolyzed with ice, saturated aqueous NH_4Cl, and 10% aqueous HCl. The separated organic solution was washed (saturated aqueous $NaHCO_3$ and water), dried, and evaporated to give a liquid residue (18.5 g), consisting of keto ester **21b**, practically pure, as a liquid: IR λ 5.75 and 5.85 μm (C=O); NMR δ 4.80 (s, 1, ArCH), 4.23 (q, 2, $COOCH_2$), 3.87 (s, 6, 2 $ArOCH_3$), 3.73 (s, 2, $COCH_2$) 1.27 (t, 3, CH_3). Anal. Calcd for $C_{20}H_{22}O_5$: C, 70.16; H, 6.48. Found: C, 70.27; H, 6.65.

Reduction of Keto Ester 21b with $NaBH_4$. A stirred solution of keto ester **21b** (1.0 g, 2.92 mmol) in EtOH (200 mL) was treated with $NaBH_4$ (1.0 g, 26.4 mmol) at room temperature. After being stirred for 2 h at the same temperature, the reaction mixture was acidified with 10% H_2SO_4 and extracted with ether. Evaporation of the washed (water, saturated aqueous $NaHCO_3$, and water) and dried ether extracts afforded a liquid residue (1.0 g) consisting of a 69:31 mixture of **22b** and **23b** (GLC), which was subjected to preparative TLC (a 74:25:1 mixture of petroleum ether, ether, and methanol was used as the eluent; elution was repeated ten times). Extraction of the two main bands (the faster moving band contained **22b**) afforded the following. Ethyl-*pref*-3-hydroxy-2,4-bis(4-methoxyphenyl)butanoate (**22b**) (0.38 g) as a liquid: IR λ 2.85 (OH), 5.85 μm (CO); NMR δ 4.43 (m, 1, C*H*OH), 3.53 (d, 1, J = 7.0 Hz, ArC*H*), 2.70 (m, 2, ArCH_2). Anal. Calcd for $C_{20}H_{24}O_5$: C, 69.75; H, 7.02. Found: C, 69.47; H, 7.18. Ethyl-*parf*-3-hydroxy-2,4-bis(4-methoxyphenyl)butanoate (**23b**) (0.12 g) as a liquid: IR λ 2.87 (OH), 5.87 μm (CO); NMR δ 4.40 (m, 1, C*H*OH), 3.55 (d, 1, J = 9.0 Hz, ArC*H*), 2.61 (m, 2, ArCH_2). Anal. Calcd for $C_{20}H_{24}O_5$: C, 69.75; H, 7.02. Found: C, 69.51; H, 7.05.

***pref*-2,4-Bis(4-methoxyphenyl)-1,3-butanediol (8b).** LAH (0.10 g) was added to a stirred solution of **22b** (0.060 g) in anhydrous ether (10 mL). After being stirred for 1 h at room temperature, the reaction mixture was refluxed for 1 h and then cooled; water and 10% aqueous NaOH were added in order to destroy the excess of hydride. The organic solution was filtered, dried, and evaporated to give a solid residue, consisting of pure diol **8b** (0.050 g), mp 138–139 °C: IR λ 3.03 μm (OH); NMR δ 4.27 (m, 1, C*H*OH), 4.08 (d, 2, J = 7.0 Hz, CH_2OH), 3.85 and 3.80 (2 s, 3 protons each, ArOCH_3), 2.93 (m, 1, ArC*H*), 2.60 (m, 2, ArCH_2). Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.24; H, 7.55.

***parf*-2,4-Bis(4-methoxyphenyl)-1,3-butanediol (9b).** Analogous LAH reduction of parf hydroxy ester **23b** (0.050 g) in anhydrous ether (7 mL), as described above for the preparation of **8b**, afforded a solid residue (0.040 g), consisting of pure **9b** as a solid, mp 76–77 °C: IR λ 3.00 μm (OH); NMR δ 4.07 (m, 3, C*H*OH and CH_2OH; this signal is partly overlapped with the ones of the two methoxy groups), 3.87 and 3.83 (2 s, 3 protons each, 2 ArOCH_3), 2.87 (m, 1, ArC*H*), 2.63 (m, 2, ArCH_2). Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.45; H, 7.27.

***pref*-4-Methoxy-1,3-bis(4-methoxyphenyl)-2-butanol (10b).** A stirred suspension of NaH (0.032 g of a 50% dispersion in oil, 0.66 mmol, washed twice with anhydrous petroleum ether) in anhydrous THF (3 mL) was heated at 50 °C and then treated dropwise with methyl iodide (0.45 g, 0.2 mL, 3.2 mmol) followed by a solution of the diol **8b** (0.20 g, 0.66 mmol) in anhydrous THF (4 mL). The resulting mixture was left at 50–55 °C for 90 min and then cooled; sufficient water was added to dissolve any precipitate. The aqueous layer was separated and extracted with ether; the ether extracts were washed (water), dried, and evaporated to give an oily residue (0.21 g), which was subjected to preparative TLC (a 50:49:1 mixture of petroleum ether, ether, and methanol was used as the eluent; elution was repeated twice). Extraction of the most intense band (R_f 0.52) afforded pure **10b** as a liquid (0.10 g): IR λ 2.88 μm (OH); NMR δ 4.20 (m, 1, C*H*OH), 3.73 and 3.70 (2 s, 3 protons each, 2 ArOCH_3), 3.70 (m, 2, CH_2O; this signal is partially overlapped by the signals of the 2 arylic methoxy groups), 3.30 (s, 3, CH_2OCH_3), 2.93 (m, 1, ArC*H*), 2.57 (m, 2, ArCH_2). Anal. Calcd for $C_{19}H_{24}O_4$: C, 72.12; H, 7.65. Found: C, 72.25; H, 7.87.

***parf*-4-Methoxy-1,3-bis(4-methoxyphenyl)-2-butanol (11b).** Analogous treatment of diol **9b** (0.10 g, 0.33 mmol) with NaH (0.016 g of a 50% dispersion in oil, 0.33 mmol) and CH_3I (0.2 mL) in anhydrous THF (4 mL), as described above for the preparation of **10b**, afforded a crude reaction product (0.10 g), which was subjected to semipreparative TLC on 0.5-mm silica gel plate (a 50:49:1 mixture of petroleum ether, ether, and methanol was used as the eluent; elution was repeated twice). Extraction of the most intense band (R_f 0.45) afforded pure **11b** (0.055 g) as an oil: IR λ 2.90 μm (OH); NMR δ 4.10 (m, 1, C*H*OH), 3.83 and 3.80 (2 s, 3 protons each, 2 ArOCH_3), 3.80 (m, 2, CH_2O; the signal is partly overlapped by the two signals of the arylic methoxy groups), 3.40 (s, 3, CH_2OCH_3), 2.93 (m, 1, ArC*H*), 2.57 (m, 2, ArCH_2). Anal. Calcd for $C_{19}H_{24}O_4$: C, 72.12; H, 7.65. Found: C, 72.33; H, 7.70.

Acid-Catalyzed Reactions of 2b and 3b in Water, Methanol, and Acetic Acid. A suspension (water) or a solution (methanol and acetic acid) of the epoxide **2b** or **3b** (0.050 g, 0.175 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 (5 mL) was stirred at 25 °C for 24 h (reaction in water), 3 h (reaction in 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 reaction mixture was previously diluted with water). Evaporation of the washed (water) ether extracts yielded mixtures consisting of diols **4b** and **5b** (reaction in water), hydroxy ethers **6b** and **7b** (reaction in methanol from cis epoxide **2b**), hydroxy ethers **6b**, **7b**, and **11b** (reaction in methanol from trans epoxide **3b**), 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 product obtained was analyzed by GLC only after saponification of the monoacetate to the corresponding diols **4b** and **5b** as described later for the reactions of **2b** and **3b** with trichloroacetic acid. The reaction of **2b** and **3b** 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.

Reactions of the Epoxide 2b and 3b 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 **2b** or **3b** (0.050 g, 0.175 mmol) in the solvent (5 mL) at 25 °C was treated with 1 M solution of trichloroacetic acid in the same solvent (0.19 mL), stirred for 3 h (reaction in CH_2Cl_2 and $CHCl_3$) or 24 h (reaction in benzene, CCl_4, and cyclohexane) at the same temperature, then washed (saturated aqueous $NaHCO_3$, and water), dried, 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 (4 mL), treated with 1 M KOH in ethanol (1.25 mL), and 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 **4b** and **5b** (together with substantial amounts of unreacted starting epoxide), which was analyzed by GLC (see Table II). Reaction of **2b** and **3b** in each solvent carried out under the same conditions, but being stopped after a longer reaction time of contact with the acid, yielded the same product composition within the experimental error. Experiments showed that the diols **4b** and **5b** are stable under the saponification conditions and that the method of saponification used does not alter the stereoselectivity of the reactions.

Acknowledgment. This work was supported in part by a grant from Consiglio Nazionale delle Ricerche (Roma) and by Ministero della Pubblica Istruzione (Roma).

Registry No. 2b, 102574-41-4; **3b**, 102574-42-5; **4b**, 63035-47-2; **5b**, 102574-43-6; **6b**, 102574-45-8; **7b**, 102574-44-7; **8b**, 102574-48-1; **9b**, 102574-49-2; **10b**, 102574-50-5; **11b**, 102574-51-6; **12**, 5703-26-4; **13**, 63035-45-0; **14b**, 63035-46-1; **15b**, 102574-40-3; **17**, 96-34-4; **18**, 42245-42-1; **19**, 84382-48-9; **20b**, 14062-18-1; **21b**, 102586-43-6; **22b**, 102574-46-9; **23b**, 102574-47-0; *p*-$CH_3OC_6H_4CHO$, 123-11-5; *i*-PrBr, 75-26-3.