T trihydrate (700 mg, 2.5 mmol) at room temperature. Workup and chromatography of the resulting oil on silica gel with benzene–AcOEt (5:1) gave **7** (497 mg, 50%) as colorless crystals: mp 132.5–134 °C (from benzene–*n*-hexane); IR ($CHCl_3$) 3350 (NH), 1330 and 1150 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.8–7.5 (m, 10, aromatic protons), 5.52, 5.15 (AB q, 1 each, J = 8 Hz, benzylic proton and NH, respectively), 2.33, 2.29, 2.18 (3 s, 3 each, 2-CH_3, 4-CH_3, and toluene ring CH_3).

Anal. Calcd for $C_{22}H_{21}NO_2S_2$: C, 66.81; H, 5.35; N, 3.54. Found: C, 66.90; H, 5.38; N, 3.56.

Further elution with the same solvent afforded **6** (377 mg, 38%) as colorless needles: mp 138–144 °C (from benzene–*n*-hexane); IR ($CHCl_3$) 1282, 1140, 1090 (SO_2), 950 (S^+–N^-) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.8–7.7 (m, 10, aromatic protons), 4.80, 3.86 (AB q, 1 each, J = 18 Hz, benzylic protons), 2.40, 2.34, 2.30 (3 s, 3 each, 2-CH_3, 4-CH_3, and toluene ring CH_3); mass spectrum, m/e (relative intensity) 395 (3.9, M^+), 239 (48), 225 (100), 224 (2.0), 211 (8.6).

Anal. Calcd for $C_{22}H_{21}NO_2S_2$: C, 66.81; H, 5.35; N, 3.54. Found: C, 66.76; H, 5.28; N, 3.59.

Thermal Isomerization of *trans*-5a. A solution of *trans*-**5a** (100 mg) in benzene (5 mL) was refluxed for 4 h and concentrated to give an equilibrium mixture of *cis*- and *trans*-**5a** in a ratio of ~3:2 by ^1H NMR spectroscopy. For the ^1H NMR spectral data of *cis*-**5a**, see Table I.

Thermal Isomerization of *trans*-5b. A solution of *trans*-**5b** (100 mg) in benzene (5 mL) was refluxed for 30 min and concentrated to give *cis*-**5b**: mp 118–120 °C (from benzene–*n*-hexane); IR ($CHCl_3$) 1280, 1160, 1080 (SO_2), 940 (S^+–N^-) cm^{-1}; ^1H NMR ($CHCl_3$) δ 6.8–7.9 (m, 10, aromatic protons), 3.78 (t, 1, J = 7.5 Hz, 9-H), 2.39, 2.36, 2.35 (3 s, 3 each, 2-CH_3, 4-CH_3, and toluene ring CH_3), 2.35 (quintet, 2, J = 7.5 Hz, 9-CH_2CH_3), 0.98 (t, 3, J = 7.5 Hz, 9-CH_2CH_3); mass spectrum, m/e (relative intensity) 423 (1.1, M^+), 394 (4.2), 253 (57), 252 (23), 225 (100).

Anal. Calcd for $C_{24}H_{25}NO_2S_2$: C, 68.05; H, 5.95; N, 3.31. Found: C, 67.78; H, 5.91; N, 3.39.

Base-Catalyzed Rearrangement of 6 with DBU. A solution of **6** (100 mg, 0.25 mmol) and DBU (40 mg, 0.25 mmol) in benzene (8 mL) was stirred at room temperature for 30 min. The mixture was diluted with benzene (10 mL), washed with 10% HCl and water, dried ($MgSO_4$), and concentrated to give a yellow solid which was recrystallized from benzene–*n*-hexane, affording **7** (90 mg, 90%).

Base-Catalyzed Rearrangement of *trans*-5a with DBU. By using a procedure similar to that described above, 2,4,9-trimethyl-9-(*N*-*p*-toluenesulfonamido)thioxanthene (**9a**) was obtained as a yellow oil from **5a** (100 mg, 0.25 mmol) and DBU (40 mg, 0.25 mmol). Because **9a** was sensitive to silica gel or alumina, the structure was based on the NMR spectrum of the crude sample of **9a** which was transformed to **10**: ^1H NMR ($CDCl_3$) δ 6.7–7.7 (m, 10, aromatic protons), 5.14 (s, 1, NH), 2.36, 2.30, 2.26 (3 s, 3 each, 2-CH_3, 4-CH_3, and toluene ring CH_3), 2.12 (s, 3, 9-CH_3).

2,4-Dimethyl-9-methylenethioxanthene (10). Crude **9a** obtained from **5a** (100 mg) was dissolved in benzene (5 mL), and silica gel (2 g) was added to the benzene solution. The reaction mixture was stirred at room temperature for 30 min. The silica gel was filtered off, and the filtrate was concentrated and chromatographed on silica gel with *n*-hexane to give **10** (38 mg, 65% from **5a**) as a light yellow oil: IR ($CHCl_3$) 1630 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.8–7.2 (m, 6, aromatic protons), 5.41 (s, 2, vinyl protons), 2.35, 2.31 (2 s, 3 each, 2- and 4-CH_3); mass spectrum, m/e 238 (M^+).

Base-Catalyzed Rearrangement of *trans*-5b. A solution of *trans*-**5b** (120 mg, 0.28 mmol) and DBU (45 mg, 0.28 mmol) in benzene (9 mL) was stirred at room temperature for 1 h. Workup and chromatography on silica gel with benzene–AcOEt (5:1) gave 9-ethyl-2,4-dimethyl-9-(*N*-*p*-toluenesulfonamido)thioxanthene (**12b**; 108 mg, 90%) as colorless crystals: mp 135–137 °C (from methanol); IR ($CHCl_3$) 3350 (NH), 1330 and 1150 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.7–7.7 (m, 10, aromatic protons), 5.77 (s, 1, NH), 2.32, 2.23, 2.05 (3 s, 3 each, 2-CH_3, 4-CH_3, and toluene ring CH_3), 0.60 (s, 3, J = 7.5 Hz, 9-CH_2CH_3). The resonance signal for the 9-methylene was masked by the three methyl signals.

Anal. Calcd for $C_{24}H_{25}NO_2S_2$: C, 68.05; H, 5.95; N, 3.31. Found: C, 68.01; H, 5.93; N, 3.31.

Base-Catalyzed Rearrangement of *cis*-5b with DBU. A solution of *cis*-**5b** (80 mg, 0.19 mmol) and DBU (30 mg, 0.19 mmol) in benzene (8 mL) was refluxed for 4.5 h. Workup gave a yellow solid which was recrystallized from methanol, giving **12b** (71 mg, 89%).

Determination of the Half-Life of 5b in $CDCl_3$ in the Presence of Piperidine as Base at 34 °C. The sample (0.25 M in substrate) was made up in NMR tubes from weighed amounts of **5b** in $CDCl_3$ with tetramethylsilane as internal standard. The NMR spectrum was then recorded, and piperidine (8.5 mg) was added. The spectrum was immediately recorded again at intervals, the temperature being held at 34 °C. The reaction was followed by electronic integration of H-9 signals.

Registry No. *cis*-**1a**, 73839-26-6; *trans*-**1a**, 73839-27-7; *cis*-**1b**, 73839-28-8; *trans*-**1b**, 73839-29-9; **4a**, 73839-30-2; **4b**, 73839-31-3; **4c**, 17394-12-6; *cis*-**5a**, 73839-32-4; *trans*-**5a**, 73839-33-5; *cis*-**5b**, 73839-34-6; *trans*-**5b**, 73839-35-7; **6**, 73839-36-8; **7**, 73839-37-9; **9a**, 73839-38-0; **10**, 73839-39-1; **12b**, 73839-40-4; methyl iodide, 74-88-4; ethyl iodide, 75-03-6.

Molecular Rearrangements. 13.[1a] Kinetics and Mechanism of Rearrangements of Some Ring-Substituted α-Chlorostyrene Oxides and *trans*-β-Chlorostyrene Oxides

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The synthesis of certain phenyl-substituted derivatives of the isomeric *trans*-β-chlorostyrene oxides (**6**) and α-chlorostyrene oxides (**7**) are reported. The kinetics of rearrangement of **6** (X = *p*-CH_3, H, *p*-Br, *m*-Cl, *p*-NO_2) to phenylchloroacetaldehydes (**12**) in CCl_4 buffered by Na_2HPO_4 and **7** (X = *p*-CH_3, H, *p*-NO_2) to ω-chloroacetophenones in CCl_4 were determined by following the rates of disappearance of the α-chloro epoxide and formation of the α-chloro carbonyl product. These substituent effects at 130 °C were correlated with σ^+ constants, yielding ρ values of −3.5 and −0.57 for the rearrangements of **6** and **7**, respectively. In nitrobenzene solvent, the $k_{C_6H_5NO_2}/k_{CCl_4}$ for **6** was 180 and for **7** was 1740, the latter solvent effect attributed to nucleophilic solvent participation. It was concluded that these thermal rearrangements of **6** and **7** occur by disrotatory C_β–O bond heterolysis to yield the corresponding α-keto carbonium–chloride ion pairs.

Early in our studies of the molecular rearrangements of α-substituted epoxides where the substituent is an electronegative atom or group, we decided to deal primarily with chlorine as that substituent. Our goal was to develop

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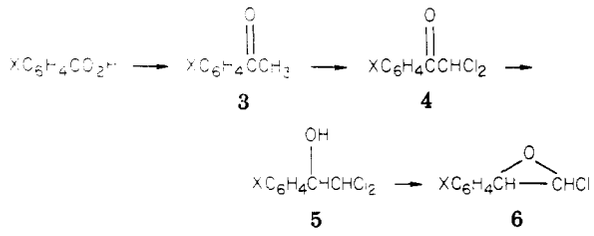
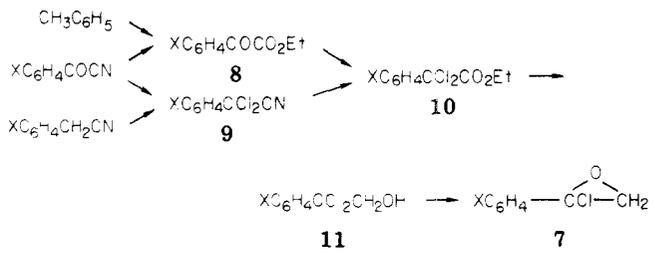
Scheme I



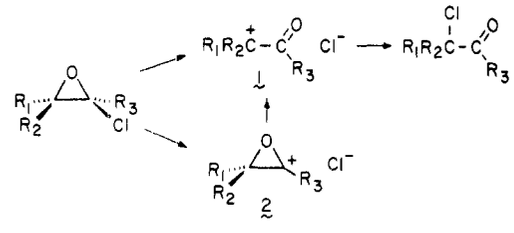
Scheme II



a reasonably clear picture of the mechanism(s) involved in such α-chloro epoxide → α-chloro carbonyl compound rearrangements in the absence of and in the presence of certain catalysts.[2]

Two of our reported results in this series have especially influenced our thinking on the mechanism of this rearrangement. The first was the neat, thermal rearrangement of a mixture of 1-chloro-*cis*- and -*trans*-4-methylcyclohexene oxides which gave *exclusively trans*-2-chloro-4-methylcyclohexanone, with *both* epoxides rearranging at the same rate.[3] The second result was the neat, thermal rerrangement of (+)-(1*R*,3*R*)-2-chloronorbornene *exo*-oxide, where the products were (−)-(1*R*,3*R*)-*exo*-3-chloronorcamphor and (+)-(1*R*,2*R*)-*exo*-2-chloro-7-ketonorbornane.[4] Each of these products results from chlorine migration and rebonding in a stereospecific manner, and the latter two products involve carbon skeleton rearrangement of the well-established 2-norbornyl cation type. Further, preliminary data on the effect of solvents on the rearrangement of 2-chlorobicyclo[2.2.2]octene oxide[5] showed a marked increase in the rate of rearrangement as solvent polarity increased.[6] A similar effect was observed in rearrangements of a steroidal α-bromo epoxide.[7]

To accommodate these and certain other features of these rearrangements, we considered two types of cation structures potentially produced in the rate-limiting step, each of which involves C–Cl bond heterolysis. One such structure was the α-keto carbonium–chloride ion pair (**1**), while the second was the oxiranyl cation–chloride ion pair (**2**). Regardless of which of these structures might be the direct product of the rate-limiting step, it was considered that the eventual products of rearrangement came from ion pair **1**.



The distinguishing feature in the formation of **1** or **2** is the site of the positive charge; in **1** this is at C_β while in **2** this site is C_α of the original α-chloro epoxide. Therefore, it appeared reasonable to test for rate-limiting formation of **1** vs. **2** by using linear free-energy relationships where R_1 or R_3, respectively, would be a substituted phenyl group.

Synthesis of Chlorostyrene Oxides. *trans*-β-Chlorostyrene Oxides. The unsubstituted *trans*-β-chlorostyrene oxide (**6**; X = H) was prepared by the procedure reported by Kirrmann and Nouri-Bimorghi[8] and is outlined in Scheme I. It was found that **6** (X = H) could be distilled at temperatures below 38 °C at 8×10^{-3} torr. No attempt was made to distill the substituted derivatives of **6**.

Chlorination of a series of commercially available acetophenones[9] produced the respective α,α-dichloro derivatives[11] [*p*-CH_3-**4** (89%), H-**4** (96%), *p*-Br-**4** (96%), *m*-Cl-**4** (99%), and *p*-NO_2-**4** (87%)]. Chlorination of *p*-CH_3O-**3** and *p*-CH_3S-**3** gave preferential ring substitution. These latter two derivatives of **4** were obtained by Friedel–Crafts dichloroacylation with dichloroacetyl chloride in chloroform[12] in modest yields. *p*-NO_2-**4** was obtained as a low-melting solid which resisted all purification procedures; it was used as such in the reduction step.

Although $LiAlH_4$[13] successfully reduced certain derivatives of **4** to **3**, $NaBH_4$[14] was more convenient in these reductions and was the preferred reagent. The resulting dichloro alcohols **5** (X = *p*-CH_3O, *p*-CH_3S, *p*-CH_3, H, *p*-Br, *m*-Cl, and *p*-NO_2) were obtained in ≥80% yields.

Reaction of several dichloro alcohols **5** with powdered potassium hydroxide in CCl_4 at temperatures between 0 and 25 °C gave the respective epoxides **6** [*p*-CH_3-**6** (26%), H-**6** (36%), *p*-Br-**6** (39%), and *m*-Cl-**6** (27%)]. The same procedure gave negligible yields of *p*-CH_3O-**6**, *p*-CH_3S-**6**, and *p*-NO_2-**6**. *p*-NO_2-**5** gave a 5–12% crude yield of *p*-NO_2-**6**, using CH_2Cl_2 as solvent. Although **6** (X = H) was depicted previously as the cis isomer,[8] we assign the trans structure to these β-chlorostyrene oxides on the basis of their vincinal proton coupling constants of 2.6–2.8 Hz.[15]

All attempts to convert *p*-CH_3O-**5** to *p*-CH_3O-**6** and *p*-CH_3S-**5** to *p*-CH_3S-**6** led to only negligible amounts of the epoxides. The NMR spectra of these crude reaction mixtures showed the presence of the *p*-substituted phenylchloroacetaldehydes, the product of rearrangement with chlorine migration.

The *trans*-β-chlorostyrene oxides, **6**, where X = H, *m*-Cl, *p*-Br, and *p*-NO_2, were purified by the method previously used to purify 2-chlorobicyclo[2.2.2]octene oxide.[5] A so-

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lution of the epoxide in CCl_4 was rapidly passed through activity III Alcoa alumina. In some cases, impurities which may have been the cis isomers contaminated the first few fractions, but these were removed in a second pass through the column. Care was taken to maintain the flow rate at >50 mL/min; otherwise, recovery of epoxide was very poor.

The more reactive epoxide *p*-CH_3-**6** was completely destroyed by even brief contact with alumina. Other adsorbants, e.g., silica gel, Florisil, and other brands of alumina, had similar effects. Since the NMR spectrum of *p*-CH_3-**6** showed no impurities other than a broadened aromatic absorption, it was assumed that the major impurity was polymeric in nature. This epoxide was purified by gel-permeation chromatography on a column of Biobeads polyethylene SX8 to give a clear, colorless solution with sharpened aromatic absorptions and no other impurities detected in the NMR spectrum.

α-Chlorostyrene Oxides. The synthetic pathways for the preparation of the substituted α-chlorostyrene oxides (**7**) are shown in Scheme II. The choice of starting reagent was ultimately dependent on the ease of preparation of intermediate **8** or **9**.

The parent ester **10** (X = H) was obtained by benzoyl cyanide alcoholysis (saturated with HCl) to keto ester **8** (X = H)[16] (67%) followed by reaction with PCl_5 to give **10**[16] (X = H) (80%). A somewhat better overall yield was obtained by SO_2Cl_2 chlorination of phenylacetonitrile to **9** (X = H) (94%) followed by alcoholysis (saturated with HCl) to **10** (X = H) (71%).

p-CH_3-**10** was prepared by the three routes shown in Scheme II. The crude yield was higher in the *p*-methylbenzoyl cyanide to *p*-CH_3-**9** conversion, compared to alcoholysis to *p*-CH_3-**8**. The yield of *p*-CH_3-**10** was lower from *p*-CH_3-**9** than that from *p*-CH_3-**8**. Following a literature report,[17] Friedel–Crafts acylation of toluene with ethyl oxalyl chloride produced *p*-CH_3-**8**. Reaction of this keto ester with PCl_5 gave *p*-CH_3-**10** in 87% yield.

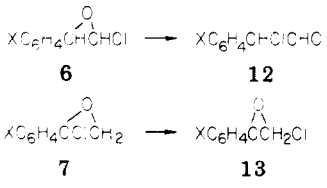
The literature warning about the "uncontrollable exothermic reaction" of *p*-nitrobenzoyl chloride and cuprous cyanide[18] led us to chlorinate (*p*-nitrophenyl)acetonitrile with aqueous sodium hypochlorite to give *p*-NO_2-**9** in 81% yield. Alcoholysis gave *p*-NO_2-**10** in 78% yield.

Reduction of the dichloro esters **10** to the alcohols **11** was accomplished with $LiAlH_4$.[19] In the reduction of *p*-NO_2-**10**, cold inverse addition was used to minimize nitro group reduction. The yields of **11** (X = H) and *p*-CH_3-**11** were nearly quantitative and 69% in the case of *p*-NO_2-**11**.

Conversion of alcohols **11** to the corresponding epoxides **7** was accomplished with base in CCl_4 instead of ether as solvent.[19] In the case of *p*-NO_2-**7** the yield was substantially improved. The yields of distilled epoxides were 81% **7** (X = H), 34% *p*-CH_3-**7**, and 65% *p*-NO_2-**7**.

Kinetic Method. The thermal instability of epoxides **6** and **7** precluded the use of GLC for analysis of these rearrangements. Of the spectral methods investigated (IR, UV, and ^1H NMR), ^1H NMR spectroscopy was selected as the most practical since the unsubstituted epoxides and their α-chloro carbonyl rearrangement products had well-defined ^1H NMR absorptions which were well-separated from neighboring absorptions. Moreover, it was felt that substituents in the phenyl ring would exhibit only minor effects on the chemical shifts of these protons used for kinetic analysis. The major disadvantages in the ^1H NMR method would be the relatively high concentrations needed (>0.05 M) and limitations in solvent choices.

The oxiranyl protons of **6** (X = H) occur at δ 5.28 (C_β-H) and 4.01 (benzylic C_α-H), and the chemical shifts of these protons remain nearly constant (±0.15 ppm) over the range of substituents examined. The major rearrangement product, phenylchloroacetaldehyde (**12**, X = H), showed ^1H NMR absorptions at δ 5.05 (benzylic C_α-H) and 9.65 (CHO). Similarly, the ^1H NMR absorption of the proton in **7** (X = H) cis to the aromatic ring at δ 2.89 was far enough removed from that of the trans proton (δ 3.32) and that of the C_α-H's of the rearrangement product, α-chloroacetophenone (**13**, X = H), to permit satisfactory analysis of epoxide loss and ketone formation.



Carbon tetrachloride and nitrobenzene were selected as a nonpolar and polar solvent, respectively, for the thermolysis rearrangement kinetic study for **6** and **7**. Since nitrobenzene solvent gave some overlap problem with the aldehydic proton of the phenylchloroacetaldehydes (**12**), nitrobenzene-d_5 was used in these studies.

It was disappointing to find that the rearrangement of **6** (X = H) was autocatalytic in the absence of an added base or buffer. A catalytic effect was also observed when various soluble amines (*sym*-collidine, triethylamine, dicyclohexylethylamine, and 1,8-bis(dimethylamino)naphthalene) were added. Four insoluble inorganic bases or buffers were tried, Na_2HPO_4, Na_2CO_3, $NaHCO_3$, and Na_2SO_3. Of these inorganics, Na_2HPO_4 gave the best agreement between the rates of epoxide disappearance and formation of aldehyde **12** (X = H). A maximum concentration of **12** (X = H) was reached which then decayed with any of these inorganic bases under the reaction conditions. This was confirmed with studies of **12** (X = H) and Na_2CO_3 or Na_2HPO_4 and probably arises by a slow aldol condensation. In separate thermolyses of **6** (X = H), 10-, 20-, and 40-mg samples of Na_2HPO_4 were added to the ampules. No change in the first-order reaction rate or point scatter was observed. This alleviated our apprehension about surface catalysis with this reagent, and it was decided to use Na_2HPO_4 in all of the kinetic studies of substituted derivatives of **6**.

A pilot study (single sealed NMR tube) of the rearrangement of **7** (X = H) with Na_2HPO_4 in CCl_4 at 90.0 °C gave first-order rate constants of 3.7×10^{-5} s^{-1} for **7** (X = H) disappearance and 3.3×10^{-5} s^{-1} for formation of **13** (X = H). However, downward curvature in the plot of log [**7**] vs. time was noted. Two further attempts to duplicate these values gave near random instantaneous rate constants. Using Na_2CO_3 in place of Na_2HPO_4 gave an initial first-order rate constant, $k \simeq 5 \times 10^{-5}$ s^{-1}, for loss of **7** (X = H), but a run containing no added base gave $k < 10^{-6}$ s^{-1}. Similar variations were observed in nitrobenzene solutions of **7** (X = H) with and without added Na_2HPO_4. Thus, these inorganic reagents catalyze the rearrangements of **7**. The approximately linear plot of log [**7**] vs. time from the pilot study using a single sealed NMR tube and the large scatter of points from the sealed-ampule method (amount of base not held constant in each tube) suggested that this catalysis may be a surface phenomenon or the result of unevenly distributed impurities in the inorganic materials. These points were not further investigated. We

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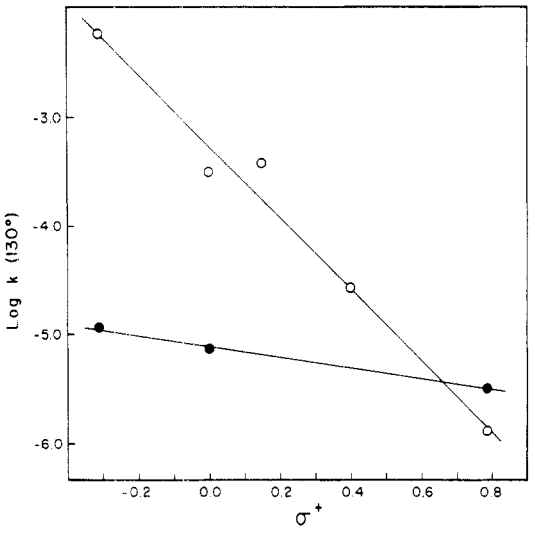


Figure 1. Plot of log k at 130 °C for **6** (○) and **7** (●) vs. σ^+ constants.

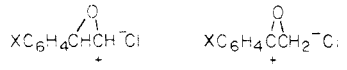
thus decided to determine the rearrangements of **7** without added base.

With the above observations, the sealed-ampule method and ^1H NMR spectral analysis were employed in the kinetic studies of the rearrangements of epoxides **6** and **7**. Solutions of the epoxide plus durene were prepared and loaded into the ampules (containing Na_2HPO_4 for runs of **6**) which were then placed into a thermostated bath for the desired time.

Rearrangement Kinetics and Mechanism. The kinetic data and calculated activation parameters for derivatives of **6** and **7** are listed in Table I. A particular problem was noted in the thermolysis of *p*-NO_2-**6**. Marked acceleration of the rate of rearrangement after $0.6t_{1/2}$ was observed, accompanied by formation of a dark red polymeric material. Using only the initial linear portion of the kinetic data gave the rate constants listed in Table I, with reasonable agreement in the k's for loss of *p*-NO_2-**6** and formation of *p*-NO_2-**12**.

The substituent effects on the rearrangements of **6** and **7** in CCl_4 at 130 °C were treated by regression analysis using several substituent constants, σ°,[20] σ,[21] and σ^+.[21] The best statistical correlations were obtained with σ^+ constants and are listed in Table II. The magnitude of ρ, however, was rather independent of the substituent constant employed. Plots of log k (disappearance) of the epoxides **6** and **7** vs. σ^+ constants are shown in Figure 1. The related plots for the formation of the carbonyl products are very similar to those shown for the disappearance of the corresponding epoxides, but are omitted for clarity.

Even though the data set of substituent effects on the rearrangement of **7** is quite limited (*p*-CH_3, H, and *p*-NO_2), it is sufficient to conclude that *aryl substituent effects have a far greater influence on the rate-limiting transition state in the rearrangement of* **6** → **12** *than they have on the* **7** → **13** *process*. If the rate-limiting step in the rearrangements of these α-chloro epoxides had involved C–Cl ionization to the corresponding oxiranyl cation–chloride ion pairs (**6** → **14** and **7** → **15**), exactly the opposite linear



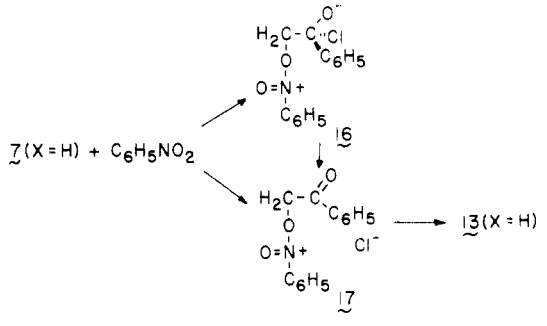
14 **15**

free-energy relationships would have been expected for these two substrate structures. In fact, the small negative ρ value found for rearrangement of **7** (ρ = –0.6) was similar to the value determined for the acetolysis of ω-diazoacetophenones (ρ = –0.82) at 40 °C where the rate-limiting step is loss of N_2 following equilibrium protonation of the diazo compound.[22] The magnitudes of the observed ρ values for **6** and **7** are also not in keeping with formation of enol hypochlorites in the rate-limiting step of rearrangement nor are the rate differences in CCl_4 and nitrobenzene.

The second probe employed in this investigation to demonstrate that ionic intermediates (possibly as ion pairs) are involved in the rate-limiting step of α-chloro epoxide rearrangements was to examine the effect of solvent on the rates. The solvents examined with the parent epoxides **6** and **7** (X = H) were CCl_4 (ϵ = 2)[23] and $C_6H_5NO_2$ (ϵ = 28).[23] These rate constants and activation parameters are listed in Table I and their relative rates in these solvents are listed in Table III.

In the rearrangement of **6**, we see a reasonable rate increase of 180-fold in the change from CCl_4 to $C_6H_5NO_2$, with essentially no change in $\Delta S^\ddagger$ in these two solvents. It was in this substrate structure **6** where a strong aryl ring substituent effect (ρ^+ = –3.5) was observed.

This same solvent change shows a more pronounced rate effect (1740) on the rearrangement of **7** (X = H), with a sharp decrease in the activation entropy, $\Delta\Delta S^\ddagger \simeq -24$ eu. In this substrate the aryl-ring substituents showed little effect on the rate-limiting step of rearrangement (ρ = –0.6). It is possible to rationalize these effects in terms of solvent participation by $C_6H_5NO_2$ at the unhindered C_β of **7** (X = H) forming a zwitterion (**16**) or ion pair (**17**) which leads



to ω-chloroacetophenone (**13**, X = H). However, the activation parameters observed with **7** (X = H) in $C_6H_5NO_2$ are very similar to those determined for the Menschutkin reaction of triethylamine and ethyl iodide in $C_6H_5NO_2$ at 100 °C; $\Delta H^\ddagger$ = 10.9 kcal/mol, $\Delta S^\ddagger$ = –39 eu.[24] We did not study the effects of [$C_6H_5NO_2$] in CCl_4 solvent on the rearrangement rate of **7** (X = H).

Due to the uncertainty of the processes involved in the rearrangement of **7** to **13** in $C_6H_5NO_2$, this data will not be considered in the "uncatalyzed" rearrangement mechanism of α-chloro epoxides. The remaining data on substituent effects in **6** and **7** in CCl_4 and the rearrangement rate acceleration of **6** in $C_6H_5NO_2$ compared to CCl_4 strongly support the formation of ionic or ion-pair intermediates with cleavage of the C_β–O bond of the α-chloro epoxide in the rate-limiting step; formation of oxiranyl cation–chloride ion pairs (**2**) has been ruled out.[25] This

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D. α,α,*m*-Trichloroacetophenone (*m*-Cl-4): materials, 9.3 g (60 mmol) of *m*-chloroacetophenone in 100 mL of HOAc; reaction temperature, 51–58 °C; time, 55 min; yield, 13.3 g (99%) of *m*-Cl-4 as a pale yellow oil; IR (neat) 1710 cm^{-1} (C=O); NMR ($CDCl_3$, Me_4Si) δ 8.22–7.23 (m, 4), 6.65 (s, $CHCl_2$, 1).

Anal. Calcd for $C_8H_5Cl_3O$: C, 42.99; H, 2.25. Found: C, 42.64; H, 2.16.

E. α,α-Dichloro-*p*-nitroacetophenone (*p*-NO_2-4): materials, 41.3 g (250 mmol) of *p*-nitroacetophenone in 125 mL of HOAc; reaction temperature, 40–54 °C; time, 1.75 h; yield, 39 g (67%) of *p*-NO_2-4 as pale yellow crystals recrystallized from 4:1 hexane–$CHCl_3$; mp 27–28 °C; IR (neat) 1720 (C=O), 1535 and 1350 cm^{-1} (NO_2); NMR ($CDCl_3$, Me_4Si) δ 8.37 (s, 4), 6.87 (s, $CHCl_2$, 1).

Anal. Calcd for $C_8H_5Cl_2O_3N$: C, 41.05; H, 2.15; N, 5.99. Found: C, 41.14; H, 2.06; N, 5.40.

Friedel–Crafts Approach to α,α-Dichloroacetophenones. A. α,α-Dichloro-4-(thiomethyl)acetophenone (*p*-CH_3S-4). To a cooled, well-stirred mixture of 13.3 g (0.1 mol) of $AlCl_3$ and 62.5 mL of $CHCl_3$ was slowly added 15 g (0.1 mol) of dichloroacetyl chloride over a period of 10 min at 0–10 °C. Thioanisole (10 g, 80 mmol) was then added dropwise with the temperature held at 0–5 °C. The mixture was allowed to warm to 20 °C and stirring was continued for 15 min. The reaction mixture was poured onto a concentrated hydrochloric acid–ice mixture, stirred, and shaken in a separatory funnel. The layers were separated, the aqueous layer was extracted twice with $CHCl_3$, and the combined $CHCl_3$ extracts were washed twice with water and dried (Na_2CO_3). Rotary evaporation of the solvent gave 14 g of a red oil which partially crystallized on cooling. The NMR spectrum suggested a mixture of 40 mol % desired ketone and 60 mol % thioanisole. Two recrystallizations from hexane gave as the major product pale yellow rhombohedral crystals and a minor product consisting of very fine pink needles in a mass on the surface of the other crystals. Mechanical separation and a further recrystallization of the major product from hexane gave 4.2 g (22.3%) of *p*-CH_3S-4 as pale yellow rhombohedral crystals: mp 69.8–70.7 °C; IR (KBr) 1680 cm^{-1} (C=O); NMR ($CDCl_3$, Me_4Si) δ 7.93 (d, *J* = 8.6 Hz, 2), 7.24 (d, *J* = 8.6 Hz, 2), 6.61 (s, $CHCl_2$, 1), 2.51 (s, SCH_3, 3).

Anal. Calcd for $C_9H_8Cl_2OS$: C, 45.97; H, 3.43. Found: C, 45.74; H, 3.53.

B. α,α-Dichloro-*p*-methoxyacetophenone (*p*-CH_3O-4). As in the synthesis of *p*-CH_3S-4 above, the materials used here were 33.3 g (0.25 mol) of $AlCl_3$, 300 mL of $CHCl_3$, 34 g (0.23 mol) of $Cl_2CHCOCl$, and 24.9 g (0.23 mol) of anisole. Removal of the solvent gave a dark oil which was dissolved in hot 2:1 EtOH–H_2O and cooled to room temperature overnight to give a mixture of white crystals and a dark oil which was decanted. Repeated recrystallization gave 14.7 g (29.2%) of *p*-CH_3O-4 as a yellow solid, mp 76.7–79.7 °C. Recrystallization from hexane gave 12.6 g (25%) of pale yellow crystals: mp 78.8–79.4 °C; IR (KBr) 1685 cm^{-1} (C=O); NMR (CCl_4, Me_4Si) δ 8.0 (d, *J* = 9.0 Hz, 2- and 6- H's, 2), 6.91 (d, *J* = 9.0 Hz, 3- and 5- H's, 2), 6.48 (s, $CHCl_2$, 1), 3.86 (s, OCH_3, 3).

Anal. Calcd for $C_9H_8Cl_2O_2$: C, 49.34; H, 3.68. Found: C, 49.49; H, 3.74.

Metal Hydride Reductions of α,α-Dichloroacetophenones. A. 1-Phenyl-2,2-dichloroethanol (5). 1. $LiAlH_4$. The literature method[13] was carried out with 95 g (0.5 mol) of **4** and gave 75 g (78%) of **5** after two recrystallizations from hexane: mp 52.8–54.1 °C (lit.[13] mp 54 °C); IR (KBr) 3425 cm^{-1} (OH); NMR (CCl_4, Me_4Si) δ 7.28 (s, 5), 5.67 (d, *J* = 5.5 Hz, $CHCl_2$, 1), 4.78 (d of d, *J* = 5.5 and 4 Hz, benzylic H, 1), 3.08 (d, *J* = 4 Hz, OH, 1).

Anal. Calcd for $C_8H_8Cl_2O$: C, 50.29; H, 4.22. Found: C, 50.48; H, 4.40.

2. $NaBH_4$. A solution of 9.54 g (0.21 mol) of 85% technical $NaBH_4$ in 120 mL of 0.02 M aqueous NaOH was added dropwise with cooling to a stirred solution of 95.0 g (0.5 mol) of **4** in 250 mL of 95% ethanol held at 5–20 °C. The mixture was allowed to warm to 28 °C during a 10-min period, stirred for 10 min, cooled, and neutralized to pH 6 with a mixture of 15 g of urea and 15 mL of acetic acid diluted to 100 mL. The mixture was brought to pH 1.5 with ca. 35 mL of 6 M sulfuric acid and extracted with three portions of ether. The combined extracts were washed twice with dilute brine and dried (Na_2SO_4). Removal of solvent using a rotary evaporator and recrystallization from 25:1 hexane–chloroform gave 66.7 g (72%) of white solid, mp 53.5–54.0 °C. Cooling of the mother liquor to 4 °C for 12 h gave 13.2 g (16.1%) of off-white product, mp 49.4–51.1 °C, the IR and NMR spectra of which were identical with those of the product from procedure 1.

B. 1-(*p*-Methylphenyl)-2,2-dichloroethanol (*p*-CH_3-5). By use of method 1, 101.6 g (0.5 mol) of *p*-CH_3-4 was reduced to *p*-CH_3-**5** isolated as a pale yellow oil which was "pure" based on its NMR spectrum. This was trap-to-trap distilled, giving 100.7 g (98%) of *p*-CH_3-**5** as a colorless oil: IR (neat) 3380 cm^{-1} (OH); NMR (CCl_4, Me_4Si) δ 7.16–6.92 (m, 4), 5.64 (d, *J* = 5.4 Hz, $CHCl_2$, 1), 4.73 (d of d, *J* = 5.4 and 4 Hz, benzylic H, 1), 3.06 (d, *J* = 4 Hz, OH, 1). Bubbling HCl into the NMR solution changed the δ 4.73 and 3.06 peaks to a doublet and a singlet, respectively.

Anal. Calcd for $C_9H_{10}Cl_2O$: C, 52.71; H, 4.92. Found: C, 52.64; H, 4.93.

C. 1-(*p*-Bromophenyl)-2,2-dichloroethanol (*p*-Br-5). By use of method 1, 10.7 g (40 mmol) of *p*-Br-4 gave 10.2 g (95%) of *p*-Br-**5** as a pale yellow oil: IR (neat) 3420 cm^{-1} (OH); NMR (CCl_4, Me_4Si) δ 7.67–7.15 (m, 4), 5.73 (d, *J* = 5.4 Hz, $CHCl_2$, 1), 4.85 (d, *J* = 5.4 Hz, benzylic H, 1), 3.34 (s, OH, 1).

Anal. Calcd for $C_8H_7BrCl_2O$: C, 35.59; H, 2.61. Found: C, 35.81; H, 2.68.

Method 2 gave a 96% yield of *p*-Br-**5**.

D. 1-(*m*-Chlorophenyl)-2,2-dichloroethanol (*m*-Cl-5). By use of method 2, 12.5 g (56 mmol) of *m*-Cl-4 gave 12.4 g (98%) of *m*-Cl-**5** as a pale yellow oil: IR (neat) 3415 cm^{-1} (OH); NMR ($CDCl_3$, Me_4Si) δ 7.48–7.09 (m, 4), 5.73 (d, *J* = 5.3 Hz, $CHCl_2$, 1), 4.87 (d, *J* = 5.3 Hz, benzylic H, 1), 3.11 (s, OH, 1).

Anal. Calcd for $C_8H_7Cl_3O$: C, 42.61; H, 3.13. Found: C, 42.66; H, 3.15.

E. 1-(*p*-Nitrophenyl)-2,2-dichloroethanol (*p*-NO_2-5). By use of method 2, 15.3 g (65 mmol) of *p*-NO_2-4 gave 10.1 g (79%) of *p*-NO_2-**5** as a pale orange solid, mp 90.1–92.9 °C. Recrystallization from CCl_4 gave fine yellow crystals: mp 92.7–93.6 °C; IR (KBr) 3460 cm^{-1} (OH); NMR ($CDCl_3$, Me_4Si) δ 8.12 (d, *J* = 8.6 Hz, 2), 7.61 (d, *J* = 8.6 Hz, 2), 5.82 (d, *J* = 4.8 Hz, $CHCl_2$, 1), 5.10 (unresolved d of d, *J* = 4.8 and 4 Hz, benzylic H, 1), 3.12 (d, *J* = 4 Hz, OH, 1).

Anal. Calcd for $C_8H_7Cl_2O_3N$: C, 40.70; H, 2.99; N, 5.93. Found: C, 40.81; H, 3.08; N, 5.86.

F. 1-(*p*-Methoxyphenyl)-2,2-dichloroethanol (*p*-CH_3O-5). By use of method 2, 14.8 g (67 mmol) of *p*-CH_3O-4 gave 14.6 g (99%) of *p*-CH_3O-**5** as a yellow oil which darkened on standing for several weeks: IR (neat) 3435 cm^{-1} (OH); NMR (CCl_4, Me_4Si) δ 7.23–6.58 (m, 4), 5.60 (d, *J* = 5.6 Hz, $CHCl_2$, 1), 4.69 (m, benzylic H, 1), 3.70 (s, OCH_3, 3), 3.44 (s, OH, 1). Addition of HCl to the NMR sample considerably sharpened the signals at δ 4.69 and 3.44 to a doublet (*J* = 5.6 Hz) and a singlet, respectively.

Anal. Calcd for $C_9H_{10}Cl_2O_2$: C, 48.89; H, 4.56. Found: C, 48.95; H, 4.56.

G. 1-(*p*-(Thiomethyl)phenyl)-2,2-dichloroethanol (*p*-CH_3S-5). By use of method 2, 3.92 g (17 mmol) of *p*-CH_3S-4 gave 3.91 g (99%) of *p*-CH_3S-**5** as a yellow oil which darkened on standing for several weeks and began to crystallize after 4 months at room temperature; each of the samples (freshly prepared and the crystals) exhibited identical NMR spectra: IR (KBr) 3400 cm^{-1} (OH); NMR (CCl_4, Me_4Si) δ 7.21 (s, 4), 6.66 (d, *J* = 5.4 Hz, $CHCl_2$, 1), 4.78 (d, *J* = 5.4 Hz, benzylic H, 1), 2.87 (s, OH, 1), 2.46 (s, SCH_3, 3).

Anal. Calcd for $C_9H_{10}Cl_2OS$: C, 45.58; H, 4.25. Found: C, 45.57; H, 4.25.

Synthesis of *trans*-β-Chlorostyrene Oxides. A. *trans*-β-Chlorostyrene Oxide (6). A solution of 7.64 g (40.0 mmol) of **5** in 50 mL of CCl_4 was cooled to −20 °C with precipitation. Powdered KOH (7.0 g, 106 mmol) was added in one portion and the mixture was stirred for 105 min while being allowed to warm to −5 °C and then for 13 h at 0 °C. The mixture was poured into 90 mL of cold water and vigorously shaken. The organic layer was separated and dried (Na_2CO_3). Rapid (>50 mL min^{-1}) chromatography with CCl_4 through 600 g of Alcoa alumina (activity III, 5% water) in an 88-mm i.d. column and concentration of the fractions using a rotary evaporator gave ca. 40 mL of a solution which was pure **6** on the basis of the NMR spectrum after storage over dibasic sodium phosphate at −25 °C for 4 days. The integrated NMR spectrum under "standard conditions"[32] indi-

Table II. Regression Analyses of Substituent Effect on Rearrangements of 6 and 7 in CCl_4 at 130.0 °C with σ^+ Constants[20]

epoxide series	disappearance of epoxide			formation of product			no. of points
	ρ	CC	F^b	ρ	CC	F^b	
6[a]	−3.5 ± 0.2	0.994	268	−3.5 ± 0.2	0.996	337	5
7	−0.57 ± 0.04	0.997	176	−0.45 ± 0.07	0.988	41	3

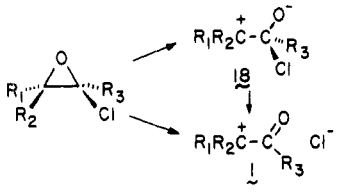
[a] Using σ°_m of Cl (0.373)[20] for *m*-Cl-6. [b] Critical value of the variance ratio test.

Table III. Effect of Solvent Change from CCl_4 to $C_6H_5NO_2$ at 70.0 °C on *k* for Epoxide Loss [6 and 7 (X = H)] and Carbonyl Product Formation [12 and 13 (X = H)]

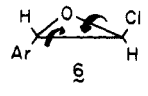
compd followed	$k_{C_6H_5NO_2}/k_{CCl_4}$
6 (X = H)	180
12 (X = H)	100[a]
7 (X = H)	1740
13 (X = H)	2140

[a] From a single determination in $C_6D_5NO_2$.

leads us to consider the formation of two types of intermediates in the rate-limiting step of rearrangement: (1) C_β–O cleavage to zwitterion 18 and (2) C_β–O cleavage in concert with C_α–Cl ionization to the α-keto carbonium–chloride ion pair (1).



The direct, concerted process from α-chloro epoxide to 1 would be related to the ionization of cyclopropyl tosylates[26] with disrotatory C_β–O bond opening, as illustrated with 6. However, the substituent effects on the rearrangements of 6 ($\rho^+ = -3.5$) and 7 ($\rho^+ = -0.6$) are quite different from those reported by DePuy[27] for the buffered acetolysis of *trans*-2-phenyl- ($\rho = -1.8$) and 1-phenylcyclopropyl tosylates ($\rho^+ = -4.3$). Schleyer et al.[28] considered that these latter data reflected formation of a classical, phenyl-stabilized, cyclopropyl cation. However, Brown et al.[29] concluded that both k_c ($\rho_c^+ = -7.1$) and k_Δ ($\rho_\Delta^+ = -2.5$) pathways were involved only with electron-releasing substituents (≥ *p*-CH_3) from 1-arylcyclopropyl ODNB solvolyses in 80% aqueous acetone. On this basis, all of the 1-arylcyclopropyl tosylate acetolysis data of DePuy et al.[27] should correspond to the k_Δ process. As expected, acetolysis of 2-arylallyl tosylates proceeded with only minor effects of aromatic substituents ($\rho^+ = -0.4$).[27]



Comparing the relative energetics for the solvolytic disrotatory opening (k_Δ) of cyclopropyl derivatives to allyl cations and of α-chloro epoxide 6 to the α-keto carbonium ion (e.g., in 1), we would expect early (less cyclopropyl ring rupture) and late (considerable epoxide C–O bond cleavage) transition-state structures, respectively, in these related processes. On the basis of this assumption, we would anticipate that the aryl substituent effects would be greater from 6 and smaller from 7, compared to those observed with the respective 2- and 1-arylcyclopropyl derivatives k_Δ solvolyses.[27,29] This is consistent with our observations. Therefore, we consider that the thermal rearrangements of α-chloro epoxides 6 and 7 proceed by disrotatory C_β–O bond opening to the α-keto carbonium–chloride ion pair 1.

Although this is perhaps an equivocal conclusion, it most directly accounts for the present data and for the stereospecific C–Cl bond formation in the α-chloro carbonyl products in cyclic[3] and bicyclic[4,5] examples. Since the Cl must migrate from one face of the α-chloro epoxide to the opposite face to yield the α-chloro ketone product (i.e., from the endo to exo faces in the norbornyl system),[4] we believe that the intermediacy of the α-keto carbonium–chloride ion pair is required in the product-forming steps of these rearrangements. The recent report that the α-cyano substituent can mesomerically stabilize a carbocation center[30] lends further support to the above conclusions.

Experimental Section[31]

Chlorination of Acetophenones to α,α-Dichloroacetophenones. A. α,α-Dichloroacetophenone (4).[11] Chlorine was bubbled into a solution of 240 g (2 mol) of acetophenone in 1 L of glacial HOAc at a rate to maintain the reaction temperature at 51–56 °C. After 4.5 h the solution was yellow and the temperature fell off sharply. The solution was poured with stirring onto 6 L of ice. The lower organic layer was dried by azeotropic distillation with 100 mL of benzene. Distillation under reduced pressure using a 30 cm × 13 mm Vigreux column gave 361.4 g (95.5%) of α,α-dichloroacetophenone: bp 130.0–131.2 °C (13 mm) [lit.[2] bp 132–134 °C (13 mm)]; IR (thin film) 1705 cm^{-1} (C=O); NMR (neat, Me_4Si) δ 7.0 (s, $CHCl_2$, 1), 7.17–8.13 (m, aromatic A_2B_2C pattern, 5).

Anal. Calcd for $C_8H_6Cl_2O$: C, 50.83; H, 3.20. Found: C, 50.43; H, 3.07.

B. α,α-Dichloro-*p*-methylacetophenone (*p*-Me-4): materials, 89.5 g (0.67 mol) of *p*-methylacetophenone in 333 mL of HOAC; reaction temperature, 47–53 °C; time, 4.0 h; yield, 120 g (89%) of *p*-Me-4 as white crystals recrystallized from hexane; mp 54.5–55.3 °C; IR (KBr) 1690 cm^{-1} (C=O); NMR (CCl_4, Me_4Si) δ 7.93 (d, *J* = 8 Hz, 2), 7.23 (d, *J* = 8 Hz, 2), 6.53 (s, $CHCl_2$, 1), 2.44 (s, CH_3, 3).

Anal. Calcd for $C_9H_8Cl_2O$: C, 53.23; H, 3.97. Found: C, 53.62; H, 4.15.

C. α,α-Dichloro-*p*-bromoacetophenone (*p*-Br-4): materials, 14.9 g (75 mmol) of *p*-bromoacetophenone in 100 mL of HOAc; reaction temperature, 53–59 °C; time, 1 h; yield, 19.2 g (96%) of *p*-Br-4 as white crystals recrystallized from hexane; mp 61.6–62 °C; IR (KBr) 1695 cm^{-1} (C=O); NMR (CCl_4, Me_4Si) δ 7.96 (d, *J* = 8.3 Hz, 2), 7.65 (d, *J* = 8.3 Hz, 2), 6.47 (s, $CHCl_2$, 1).

Anal. Calcd for $C_8H_5BrCl_2O$: C, 35.86; H, 1.88. Found: C, 35.82; H, 2.04.

(25) It should also be pointed out that the pronounced solvent effect (CCl_4 and $C_6H_5NO_2$) on the rate of rearrangement of 6 to 12 does not support formation of an enol hypochlorite in the rate-limiting step or a fully concerted, one-step rearrangement.

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(31) Melting points were determined on a Kofler hot stage and are uncorrected, as are boiling points. Spectra were obtained on commercial instruments (IR, Perkin-Elmer 137; NMR, Varian T-60). GLC analyses were recorded with a Hewlett-Packard 5750 instrument fitted with a disc integrator.

Table I. Rate Constants and Activation Parameters for Rearrangement of Substituted α-Chlorostyrene Oxides (7) and *trans*-β-Chlorostyrene Oxides (6)

					disappearance of epoxide				formation of carbonyl product[c]			
epoxide	solvent	concn, M	temp, °C	base	$10^5 k_{obsd}$, s^{-1}	$10^5 k_{av}$, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	$10^5 k_{obsd}$, s^{-1}	$10^5 k_{av}$, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
6 (X = H)	CCl_4	0.34	70.0	Na_2CO_3	0.125 ± 0.005[a]	0.129			0.079 ± 0.008	0.076		
					0.132 ± 0.003				0.073 ± 0.004			
6 (X = H)	CCl_4	0.34	90.0	Na_2CO_3	1.01 ± 0.02	1.01	24.7	−13.7	0.617 ± 0.040	0.612	24.5	−15.4
					1.02 ± 0.02				0.607 ± 0.033			
6 (X = H)	CCl_4	0.28	110.0	Na_2CO_3	6.45 ± 0.10	6.36			3.97 ± 0.27	3.61		
					6.28 ± 0.09				3.25 ± 0.26			
6 (X = H)	CCl_4	0.29	70.0	Na_2HPO_4	0.166 ± 0.001	0.116			0.100 ± 0.002	0.101		
					0.117 ± 0.001				0.101 ± 0.002			
6 (X = H)	CCl_4	0.29	90.0	Na_2HPO_4	0.908 ± 0.008	0.905	24.9	−13.5	0.807 ± 0.009	0.806	25.2	−12.7
					0.901 ± 0.012				0.805 ± 0.015			
6 (X = H)	CCl_4	0.29	110.0	Na_2HPO_4	5.60 ± 0.07	5.83			5.47 ± 0.06	5.38		
					6.06 ± 0.06				5.28 ± 0.13			
6 (X = H)	CCl_4		130.0	Na_2HPO_4		(30.9)[b]				(29.1)[b]		
p-CH_3-6	CCl_4	0.28	70.0	Na_2HPO_4	3.33 ± 0.06	3.26	23.3	−11.5	3.28 ± 0.06	3.24	22.3	−14.5
					3.20 ± 0.04				3.20 ± 0.04			
p-CH_3-6	CCl_4	0.27	90.0	Na_2HPO_4	22.6 ± 0.3	22.6			21.5 ± 0.4	20.7		
					22.6 ± 0.5				19.8 ± 0.6			
p-CH_3-6	CCl_4		130.0	Na_2HPO_4		(615)[b]				(490)[b]		
p-Br-6	CCl_4	0.21[a]	90.0	Na_2HPO_4	0.670 ± 0.010	0.671	28.5	−4.1	0.594 ± 0.015	0.595	27.0	−8.5
					0.671 ± 0.014				0.595 ± 0.017			
p-Br-6	CCl_4	0.40	120.0	Na_2HPO_4	14.6 ± 0.1	14.8			10.9 ± 0.4	11.2		
					15.0 ± 0.1				11.5 ± 0.2			
p-Br-6	CCl_4		130.0	Na_2HPO_4		(37.5)[b]				(27.1)[b]		
m-Cl-6	CCl_4	0.34	130.0	Na_2HPO_4	2.69 ± 0.02	2.75			1.91 ± 0.09	1.94		
					2.80 ± 0.04				1.97 ± 0.07			
p-NO_2-6	CCl_4	0.23	130.0	Na_2HPO_4	0.132 ± 0.012				0.117 ± 0.005			
6 (X = H)	$O_2NC_6H_5$	0.43	50.0	Na_2HPO_4	2.79 ± 0.03	2.79	21.6	−12.6				
					2.79 ± 0.03							
6 (X = H)	$O_2NC_6H_5$	0.26	70.0	Na_2HPO_4	21.1 ± 0.2	21.1						
					21.2 ± 0.2							
6 (X = H)	$O_2NC_6H_5$	0.38	70.0	Na_2HPO_4	22.4 ± 0.2				10.2 ± 0.6			
7 (X = H)	CCl_4		70.0	none		(0.0021)[b]				(0.0017)[b]		
7 (X = H)	CCl_4	0.40	130.0	none	0.794 ± 0.026	0.764	26.4	−17.1	0.716 ± 0.035	0.739	27.1	−15.5
					0.734 ± 0.027				0.762 ± 0.031			
7 (X = H)	CCl_4	0.39	150.0	none	4.09 ± 0.17	3.80			3.97 ± 0.15	3.83		
					3.50 ± 0.17				3.69 ± 0.20			
p-CH_3-7	CCl_4	0.44	130.0	none	1.18 ± 0.01	1.18	23.5	−23.5	1.07 ± 0.04	1.14	23.5	−23.4
					1.19 ± 0.02				1.21 ± 0.04			
p-CH_3-7	CCl_4	0.35	150.0	none	4.78 ± 0.33	4.94			4.63 ± 0.37	4.80		
					5.10 ± 0.21				4.95 ± 0.30			
p-NO_2-7	CCl_4	0.34	130.0	none	0.268 ± 0.045	0.309	25.2	−22.0	0.371 ± 0.021	0.384	21.3	−31.0
					0.350 ± 0.020				0.397 ± 0.015			
p-NO_2-7	CCl_4	0.37	150.0	none	1.43 ± 0.03				1.42 ± 0.07			
7 (X = H)	$O_2NC_6H_5$	0.36	50.0	none	1.04 ± 0.05	1.05	13.1	−41.1	1.02 ± 0.05	1.03	13.3	−40.5
					1.06 ± 0.05				1.04 ± 0.05			
7 (X = H)	$O_2NC_6H_5$	0.36	70.0	none	3.60 ± 0.13	3.65			3.59 ± 0.12	3.64		
					3.70 ± 0.10				3.70 ± 0.12			

[a] Calculated slope deviation at 95% confidence level. [b] Extrapolated from data at different temperatures. [c] Formation rate constants were calculated with a theoretical infinity point with product concentration equal to the sum of the initial epoxide and product concentrations.

cated the solution was 0.36 M (36% yield). The IR and NMR spectra were in agreement with those reported in the literature.[8] As reported,[8] attempts to isolate **6** for elemental analysis led to partial rearrangement to **12**.

B. *trans*-β-Chloro-*p*-methylstyrene Oxide (*p*-CH_3-6). From 10.3 g (0.05 mol) of *p*-CH_3-**5** in 75 mL of CCl_4 stirred for 22 h at 3.5 °C with 11.1 g (0.17 mol) of KOH was obtained a brown solution. The solvent was almost completely removed with a rotary evaporator, and the crude product was mixed thoroughly with 50 mL of hexane and cooled to −25 °C for 36 h. The yellow supernatant liquid was decanted and dried ($NaCO_3$). The hexane was removed completely with the rotary evaporator followed by agitating under reduced pressure (0.1 mm) for 5 min. The yellow product was dissolved in 50 mL of CCl_4 and examined by NMR spectroscopy under "standard conditions".[32] The solution was 0.29 M in *p*-CH_3-**6** with no other absorptions outside the aromatic region. The solution was chromatographed on a 16 mm × 1 m column of 200/400 mesh Biobeads SX8 (packed with benzene and thoroughly washed with carbon tetrachloride). After a yellow forerun, 45 mL of colorless epoxide solution which was 0.29 M in *p*-CH_3-**6**, on the basis of the integrated NMR spectrum with no other absorptions, was obtained, corresponding to a 26% yield of *p*-CH_3-**6**: NMR (CCl_4, Me_4Si) δ 7.17 (s, 4), 5.23 (d, J = 2.6 Hz, $C_\beta H$, 1), 3.96 (d, J = 2.6 Hz, 1), 2.40 (s, 3).

C. *trans*-β-Chloro-*p*-bromostyrene Oxide (*p*-Br-6). From a mixture of 8.7 g (32 mmol) of *p*-Br-**5** and 8.6 g (130 mmol) of powdered KOH in 190 mL of CCl_4 stirred by tumbling in a rotating flask at 0 °C, there was obtained after alumina chromatography 24.5 mL of a CCl_4 solution 0.51 M[32] in *p*-Br-**6**: NMR (CCl_4, Me_4Si) δ 7.32 (m, 4), 5.30 (d, J = 2.8 Hz, $C_\beta H$, 1), 3.98 (d, J = 2.8 Hz, 1).

D. *trans*-β-Chloro-*m*-chlorostyrene Oxide (*m*-Cl-6). As in the synthesis of **6**, 9.25 g (41 mmol) of *m*-Cl-**5** and 13 g (20 mmol) of powdered KOH in 55 mL of CCl_4 stirred at 0 °C for 7.5 h after alumina chromatography gave 17.9 mL of a 0.6 M solution[32] of *m*-Cl-**6** (27%): NMR (CCl_4, Me_4Si) δ 7.35 (m, 4), 5.35 (d, J = 2.6 Hz, $C_\beta H$, 1), 4.09 (d, J = 2.6 Hz, 1).

E. *trans*-β-Chloro-*p*-nitrostyrene Oxide (*p*-NO_2-6). A suspension of 0.68 g (6 mmol) of resublimed KO-*t*-Bu in 40 mL of ether was added to a stirred solution of 1.42 g (6 mmol) of *p*-NO_2-**5** in 400 mL of ether at −15 °C. The temperature rose to −5 °C and the color became light purple. After the mixture was stirred for 1.6 h, the temperature was allowed to rise to 20 °C. Ice and water were added, the mixture was shaken, and the layers were separated. The ether layer was washed with three 100-mL portions of dilute brine. The dark red ether solution was dried (Na_2CO_3) and evaporated to near dryness with a rotary evaporator. The residue was extracted with 50-, 40-, 20-, and 10-mL portions of CCl_4. The combined extracts were washed with dilute brine, dried (Na_2CO_3), and concentrated to 7.0 mL with a rotary evaporator. NMR spectral analysis[32] showed the yield of *p*-NO_2-**6** to be 12%. Chromatography on activity III alumina removed traces of starting alcohol to give *p*-NO_2-**6**: NMR (CCl_4, Me_4Si) δ 8.20 (d, J = 8.2 Hz, 2), 7.49 (d, J = 8.2 Hz, 2), 5.35 (d, J = 2.8 Hz, $C_\beta H$, 1), 4.16 (d, J = 2.8 Hz, 1).

Ethyl Phenyldichloroacetate (10, X = H). A mixture of 5.35 g (30 mmol) of ethyl phenylglyoxylate and 6.25 g (30 mmol) of PCl_5 was heated in steps of 20 °C to 95 °C with stirring and stirred for 1 h at 97 ± 2 °C. The mixture was cooled and fractionally distilled under reduced pressure on a platinum spinning-band column to give 5.58 g (79.9%) of **10** (X = H) as a colorless oil: bp 97–103 °C (2.0 mm) (lit.[16] bp 263–266 °C); IR (thin film) 1755 cm^{-1} (C=O); NMR (CCl_4, Me_4Si) δ 7.77–7.14 (m, 5), 4.22 (q, J = 7 Hz, CH_2, 2), 1.23 (t, J = 7 Hz, CH_3, 3).

Anal. Calcd for $C_{10}H_{10}Cl_2O_2$: C, 51.53; H, 4.32. Found: C, 51.53; H, 4.15.

2-Phenyl-2,2-dichloroethanol (11, X = H). **10** (X = H, 37.3 g, 0.16 mol) was reduced with $LiAlH_4$ according to the literature procedure[19] to give 30.2 g (99%) of a yellow oil which solidified when stored at −25 °C for 12 h. The material remained solid upon storage at room temperature for 24 h but had undergone ca. 20% conversion to phenylchloroacetaldehyde based on the integrated NMR spectrum. The freshly prepared sample was pale yellow: mp 37.0–41.5 °C; NMR ($CDCl_3$, Me_4Si) δ 7.86–7.12 (m, 5), 4.03 (s, CH_2, 2), 3.48 (s, OH, 1). The *p*-nitrobenzoate was prepared and recrystallized from ethanol to give pale yellow crystals, mp 69.4–70.2 °C.

Anal. Calcd for $C_{15}H_{11}Cl_2NO_4$: C, 52.96; H, 3.26; N, 4.12. Found: C, 53.11; H, 3.32; N, 4.11.

α-Chlorostyrene Oxide (7, X = H). A solution of 9.56 g (50 mmol) of **11** (X = H) in 120 mL of CCl_4 was stirred for 75 min at 0 °C with 20 mL of 10% aqueous NaOH (50 mmol). The organic layer was dried (Na_2CO_3), concentrated to 20 mL with a rotary evaporator, and trap-to-trap distilled at room temperature (10^{-3} mm) with Na_2HPO_4 in the distilling and receiving flasks. Dilution to 90.0 mL with purified CCl_4 gave a solution 0.45 M in **7** (X = H)[32] with no extraneous peaks in the NMR spectrum. The yield was 40.5 mmol (81%). Rotary evaporation of the solvent gave a colorless oil: IR (neat) 1210, 920, 832 cm^{-1} (epoxide ring); NMR (CCl_4, Me_4Si) δ 7.63–7.14 (m, 5), 3.32 (d, J = 6 Hz, 1), 2.89 (d, J = 6 Hz, 1).

Anal. Calcd for C_8H_7ClO: C, 62.15; H, 4.56. Found: C, 62.26; H, 4.60.

Ethyl *p*-Tolylglyoxylate (*p*-CH_3-8). Ethyl oxalyl chloride (25.0 g, 183 mmol) was added over a period of 30 min to a stirred, cold mixture of 25.2 g (189 mmol) of $AlCl_3$, 36.6 g (29 mL) of CS_2 (distilled from P_2O_5), and 19.4 g (210 mmol) of toluene at a bath temperature of 0 °C and stirred at 0 °C for 1.0 h. The mixture was allowed to warm and stirred at ca. 30 °C for 3 h, at which time the viscosity of the red mixture precluded further stirring. Some of the product was scraped into a mixture of 300 mL of ice and 10 mL of concentrated hydrochloric acid. The aqueous portion of the resulting mixture was poured into the reaction flask. The ensuing vigorous reaction caused some product to be spilled. When hydrolysis was complete, the mixture was extracted with two 50-mL portions of ether. The combined organic layers were washed with two 25-mL portions of dilute brine and dried ($MgSO_4$). Removal of solvent using a rotary evaporator gave 27.2 g of oil–solid mixture. Addition of 20 mL of CCl_4, storage at −25 °C overnight, and filtration gave 5.4 g of impure acid which the IR and NMR spectra suggested was (*p*-methylphenyl)glyoxylic acid. Removal of solvent from the filtrate using a rotary evaporator gave 22.5 g of impure *p*-CH_3-**8** containing ca. 24% *p*-tolylglyoxylic acid on the basis of the integrated NMR spectrum. The crude ester was dissolved in an equal volume of ether and washed with two 15-mL portions of saturated $NaHCO_3$ solution. The organic layer was dried ($MgSO_4$), and the solvent was removed with a rotary evaporator to give 15.4 g (43.8%) of yellow oil which contained none of the acid on the basis of the NMR spectrum. Additional *p*-tolylglyoxylic acid (3.6 g) was recovered from the acidified bicarbonate wash. The ester solidified upon storage at −25 °C: IR (neat) 1745 and 1690 cm^{-1} (C=O's); NMR ($CDCl_3$, Me_4Si) δ 8.01–7.73 (m, 2), 7.43–7.12 (m, 2), 4.40 (q, J = 7 Hz, CH_2, 2), 2.41 (s, CH_3, 3), 1.39 (t, J = 7 Hz, CH_3, 3).

Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.30. Found: C, 68.67; H, 6.34.

Ethyl *p*-Tolyldichloroacetate (*p*-CH_3-10). A mixture of 14.4 g (75 mmol) of *p*-CH_3-**8** and 15.7 g (75 mmol) of PCl_5 was warmed to 95 °C with stirring over a period of 40 min and stirred at 97 ± 2 °C for 90 min. Distillation on a spinning-band column gave, after a forerun of $POCl_3$, 16.1 g (86.7%) of *p*-CH_3-**10** as a colorless oil: bp 83 °C (0.28 mm) to 97 °C (0.45 mm); IR (neat) 1745 cm^{-1} (C=O); NMR ($CDCl_3$, Me_4Si) δ 7.73–7.02 (m, 4), 4.26 (q, J = 7.2 Hz, CH_2, 2), 2.35 (s, CH_3, 3), 1.25 (t, J = 7.2 Hz, CH_3, 3).

Anal. Calcd for $C_{10}H_{12}Cl_2O_2$: C, 53.46; H, 4.90. Found: C, 53.56; H, 4.94.

2-(*p*-Tolyl)-2,2-dichloroethanol (*p*-CH_3-11). A solution of 14.1 g (57.0 mmol) of *p*-CH_3-**10** in 16 mL of dry ether was added dropwise over a period of 55 min with stirring and external cooling to a suspension of 1.35 g (35.6 mmol) of $LiAlH_4$ in ca. 30 mL of dry ether maintained at −15 to −3 °C. After being stirred for 15 min at 0 ± 2 °C, the reaction mixture was worked up[19] to give 11.3 g (97%) of *p*-CH_3-**11** as a yellow oil: IR (neat) 3320 cm^{-1} (OH); NMR ($CDCl_3$, Me_4Si) δ 7.61–6.98 (m, 4), 4.05 (s, CH_2, 2), 3.53 (s, OH, 1), 2.32 (s, CH_3, 3). The *p*-nitrobenzoate ester was prepared and recrystallized from ethanol to give pale yellow needles, mp 80.8–81.8 °C.

(32) The "standard conditions" referred to involved successive NMR integration of the resonances of the durene standard (CH_3), the upfield epoxide proton, and the aldehyde (CHO) or ketone (CH_2Cl) protons with predetermined best-settings on the T-60 spectrometer.

Anal. Calcd for $C_{16}H_{13}Cl_2NO_4$: C, 54.25; H, 3.70; N, 3.96. Found: C, 54.38; H, 3.79; N, 3.93.

α-Chloro-*p*-methylstyrene Oxide (*p*-CH_3-7). As in the synthesis of epoxide 7 (X = H), 10.8 g (53 mmol) of *p*-CH_3-**10** in 135 mL of CCl_4, and 2.4 g (60 mmol) of NaOH in 28 mL of water were stirred together at 0 °C for 40 min. After workup, 180 mL of a 0.15 M *p*-CH_3-**7** solution in CCl_4 was obtained[32] which was concentrated to 40 mL (0.443 M in *p*-CH_3-**7**; 34% yield). A portion of this solution was evaporated to dryness for analysis: IR (neat) 1200 and 820 cm^{-1}; NMR (CCl_4, Me_4Si) δ 7.48–6.98 (m, 4), 3.30 (d, J = 6 Hz, 1), 2.86 (d, J = 6 Hz, 1), 2.36 (s, CH_3, 3).

Anal. Calcd for C_9H_9ClO: C, 64.10; H, 5.38. Found: C, 64.24; H, 5.46.

(*p*-Nitrophenyl)dichloroacetonitrile (*p*-NO_2-9). A solution of 40.54 g (250 mmol) of (*p*-nitrophenyl)acetonitrile in 500 mL of $CHCl_3$ was vigorously stirred with 1000 mL of 5.25% NaOCl (Clorox) (700 mmol) for 7 min at 25–38 °C. Most of the aqueous layer was removed by suction pipet. Water (900 mL) was added and the mixture was stirred for 1 min. Most of the aqueous layer was removed by suction pipet, and the remaining mixture was filtered with suction. The layers were separated, the organic layer was washed with 250 mL of water in a separatory funnel and dried ($MgSO_4$), and the solvent was removed with a rotary evaporator to give 47.7 g of a yellow oil containing some solid. Suction filtration gave 46.6 g of yellow *p*-NO_2-**9**: IR (neat) 1530 and 1350 cm^{-1} (NO_2); NMR ($CDCl_3$, Me_4Si) δ 8.53–7.88 (m, aromatic).

Anal. Calcd for $C_8H_4Cl_2N_2O_2$: C, 41.59; H, 1.75; N, 12.13. Found: C, 41.62; H, 1.79; N, 12.26.

Ethyl (*p*-Nitrophenyl)dichloroacetate (*p*-NO_2-10). A solution of 43.8 g (190 mmol) of *p*-NO_2-**9** in 90 mL of 95% ethanol and 50 mL of absolute ethanol saturated with dry HCl was stirred at 0–4 °C for 103 h. Workup produced 49.8 g of a dark yellow oil. Addition of four volumes of a 3:5 v/v mixture of pentane–CH_2Cl_2 gave a precipitate. Removal of solvent using a rotary evaporator followed by slow suction filtration gave 47.0 g of orange oil. Trap-to-trap distillation (2×10^{-4} mm; bath temperature 123–149 °C) gave 44.0 g of light yellow solid. Recrystallization from several solvents (hexane, $CHCl_3$, hexane–$CHCl_3$, and CH_2Cl_2) gave 41.1 g (77.9%) of yellow crystals: mp 34.0–36.9 °C; IR (melt) 1760 (C=O), 1530 and 1350 cm^{-1} (NO_2); NMR ($CDCl_3$, Me_4Si) δ 8.43–7.73 (m, 4), 4.32 (q, J = 7.1 Hz, CH_2, 2), 1.39 (t, J = 7.1 Hz, CH_3, 3).

Anal. Calcd for $C_{10}H_9Cl_2NO_4$: C, 43.19; H, 3.26; N, 5.04. Found: C, 43.24; H, 3.36; N, 5.05.

2-(*p*-Nitrophenyl)-2,2-dichloroethanol (*p*-NO_2-11). To a stirred solution of 25.0 g (90 mmol) of *p*-NO_2-**10** in 400 mL of dry ether held at 0–4 °C was added over a period of 7.25 h a solution of 2.28 g (60 mmol) of $LiAlH_4$ in 400 mL of dry ether. The mixture was stirred at 2 °C for 15 min and then acidified to pH <4 with cold 20% sulfuric acid. The ethereal layer was washed with two 200-mL portions of dilute brine and dried ($MgSO_4$), and the solvent was removed with a rotary evaporator to give 20.4 g *p*-NO_2-**11** as an orange solid. Recrystallization from $CHCl_3$ gave 14.7 g (69%) of *p*-NO_2-**11** as pale yellow crystals: mp 87.6–88.6 °C; IR (KBr) 3485 (OH), 1515 and 1350 cm^{-1} (NO_2); NMR ($CDCl_3$, Me_4Si) δ 8.37–7.77 (m, 4), 4.23 (s, CH_2, 2), 2.78 (s, OH, 1).

Anal. Calcd for $C_8H_7Cl_2NO_3$: C, 40.70; H, 2.99; N, 5.93. Found: C, 40.66; H, 3.07; N, 5.90.

α-Chloro-*p*-nitrostyrene Oxide (*p*-NO_2-7). A hot solution of 2.95 g (12.5 mmol) of *p*-NO_2-**11** in 55 mL of CCl_4 was rapidly cooled to 0 °C with stirring. To the fine suspension was added with stirring 750 mL of 1% aqueous NaOH (187.5 mmol) precooled to 0 °C. The mixture was stirred vigorously for 27 min at 0 °C and poured into a cold separatory funnel, and the layers were separated. The organic layer was washed with 25 mL of water, dried (Na_2CO_3), and filtered to give 144.4 g of clear solution which was 0.105 M in *p*-NO_2-**7**. Removal of solvent using a rotary evaporator followed by recrystallization to 0 °C from a minimum amount of pentane gave 1.63 g (65.3%) of very pale yellow crystals: mp 44.5–48.5 °C dec; IR (KBr) 1515 and 1340 (NO_2), 1205 and 852 cm^{-1} (epoxide ring); NMR (CCl_4, Me_4Si) δ 8.26 (d, J = 9.3 Hz, 2), 7.69 (d, J = 9.3 Hz, 2), 3.45 (d, J = 5.8 Hz, 1), and 2.96 (d, J = 5.8 Hz, 1).

Anal. Calcd for $C_8H_6ClNO_3$: C, 48.14; H, 3.03; N, 7.02. Found: C, 48.04; H, 3.10; N, 6.99.

Preparation of Solutions for Kinetic Studies. For epoxides **6** the CCl_4 solutions were prepared directly from the column chromatography eluates. The fractions in which no impurities were evident by NMR spectroscopy were combined and diluted to the appropriate concentration with distilled CCl_4. The CCl_4 was removed on a rotary evaporator followed by pumping at 0.1 mm for 5 min at room temperature to prepare the nitrobenzene solutions. The appropriate amount of purified nitrobenzene[33] was then added. To each solution was added zone-refined durene (5 mg/mL) as an internal proton standard.

With the epoxides **7**, the freshly distilled or recrystallized epoxide was dissolved in the appropriate purified solvent and the internal proton standard, durene, was added.

Kinetic Method. The sealed ampule technique was used in these studies. The 2-mL Kimble Neutraglas ampules were cleaned with 50% aqua regia, distilled water, 20% NH_4OH, and distilled water, dried in a 120 °C oven, and stored in a desiccator under dry N_2. Where insoluble bases were used, the base was added to the ampule first and the dry ampule was tapped to free the ampule neck of any solid particles. The solutions of **6** or **7** were then added with a constant delivery pipet with a long thin tip. The filled ampules were cooled in liquid N_2, pumped down to 0.1 mm, and sealed with a torch. The sealed ampules were placed in an ampule rack with each ampule held in the rack by a wire. The rack was completely immersed in a constant temperature bath and turned on its long axis by a motor–chain drive mechanism. This produced effective mixing in each ampule, especially required for those samples containing an insoluble base.

The ampules were removed at various times, quenched in cold baths, and maintained cold until a kinetic run was complete. The ampules were opened (after centrifugation for those containing insoluble bases) and the solution was analyzed by successive NMR integration of the durene methyl resonance, the upfield epoxide protons, and the aldehyde or ketone protons.[32] After the numbers of protons in a particular resonance were corrected for, these integral heights over 10 scans were averaged.

Rate constants were calculated with a computer program NMRKIN1, an abridged version of RATSOL2,[34] for calculating first-order rate constants from readings proportional to substrate concentration; initial concentrations of **6** or **7** were used.

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Registry No. **4** (X = H), 2648-61-5; **4** (X = *p*-CH_3), 4974-59-8; **4** (X = *p*-Br), 7716-86-1; **4** (X = *m*-Cl), 4252-78-2; **4** (X = *p*-NO_2), 16208-23-4; **4** (X = *p*-CH_3S), 73805-16-0; **4** (X = *p*-CH_3O), 29003-60-9; **5** (X = H), 2612-36-4; **5** (X = *p*-CH_3), 17936-67-3; **5** (X = *p*-Br), 61693-77-4; **5** (X = *m*-Cl), 27683-61-0; **5** (X = *p*-NO_2), 35996-51-1; **5** (X = *p*-CH_3O), 58622-56-3; **5** (X = *p*-CH_3S), 73805-17-1; **6** (X = H), 73805-18-2; **6** (X = *p*-CH_3), 73805-19-3; **6** (X = *p*-Br), 73805-20-6; **6** (X = *m*-Cl), 73805-21-7; **6** (X = *p*-NO_2), 73805-22-8; **7** (X = H), 1194-34-9; **7** (X = *p*-CH_3), 73805-23-9; **7** (X = *p*-NO_2), 73805-24-0; **8** (X = *p*-CH_3), 5524-56-1; **9** (X = *p*-NO_2), 73805-25-1; **10** (X = H), 5317-66-8; **10** (X = *p*-CH_3), 73805-26-2; **10** (X = *p*-NO_2), 73805-27-3; **11** (X = H), 1125-24-2; **11** (X = *p*-CH_3), 73805-28-4; **11** (X = *p*-CH_3) *p*-nitrobenzoate ester, 73805-29-5; **11** (X = *p*-NO_2), 73805-30-8; **12** (X = H), 4638-79-3; **13** (X = H), 532-27-4; acetophenone, 98-86-2; *p*-methylacetophenone, 122-00-9; *p*-bromoacetophenone, 99-90-1; *m*-chloroacetophenone, 99-91-2; *p*-nitroacetophenone, 100-19-6; dichloroacetyl chloride, 79-36-7; thioanisole, 100-68-5; anisole, 100-66-3; ethyl phenylglyoxylate, 1603-79-8; ethyl oxalyl chloride, 4755-77-5; toluene, 108-88-3; *p*-tolylglyoxylic acid, 7163-50-0; (*p*-nitrophenyl)acetonitrile, 555-21-5; **11** (X = H) *p*-nitrobenzoate, 73805-31-9.

(33) K. B. Wiberg, "Laboratory Techniques in Organic Chemistry", McGraw-Hill, New York, 1960, p 251.

(34) R. N. McDonald and G. E. Davis, *J. Org. Chem.*, **38**, 138 (1973).