phenoxy-1-phenylbutan-2-one (**15**): λ_{max}^{film} 5.80 μ (C=O), 6.67 (Ph), 8.09 (Ph—O), 13.26 and 14.45 (Ph); $\delta_{TMS}^{CDCl_3}$ 1.40 (d, 3, CH_3, J = 7.0 Hz), 3.80 (2, CH_2), 4.67 (q, 1, CH, J = 6.65 Hz), 6.7–7.1 (m, 5, OPh), 7.16 (5, Ph); $n^{25}D$ 1.5493; bp 161–165° (0.3 mm).

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.12; H, 6.45.

The minor product with the slightly shorter retention time was identified as 1-phenoxy-1-phenylbutan-2-one (**14**): λ_{max}^{film} 5.80 μ (C=O); $\delta_{TMS}^{CDCl_3}$ 0.90 (t, 3, CH_3, J = 7.0 Hz), 2.56 (q, 2, CH_2, J = 7.0 Hz), 5.57 (1, CH), 6.7–7.1 (m, 5, OPh), 7.16 (5, Ph); $n^{25}D$ 1.5540; bp 145–148° (0.3 mm).

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.52; H, 6.74.

Reaction of 1-Chloro-1-phenylbutan-2-one (7) with 0.05 *M* Sodium Phenoxide in Phenol. The reaction of 0.50 g (2.7 mmol) of **7** with 110 ml of 0.05 *M* sodium phenoxide (5.5 mmol) in phenol was carried out under the standard Favorskii reaction conditions. The reaction was stirred for 3.5 hr at 50° before work-up. The 0.64 g (97%) of product was shown by nmr, ir, and vpc peak enhancement to be the isomeric phenoxy ketones: **14**, 18% and **15**, 82%.

Reaction of 1-Chloro-1-phenylbutan-2-one (7) with 0.05 *M* Sodium Phenoxide in Phenol, Inverse Addition Procedure. A 0.05 *M* solution of sodium phenoxide in phenol (50 ml) was added dropwise over a period of 4 hr to 0.50 g (2.7 mmol) of **7** in 100 ml of phenol at 50°. The 0.62 g (96%) of product was shown by nmr, ir, and vpc peak enhancement to be the isomeric phenoxy ketones: **14**, 18% and **15**, 82%.

Reaction of 1-Chloro-1-phenylbutan-2-one (7) with 0.05 *M* Base and 0.05 *M* Phenol in Methanol. The reaction of 0.50 g (2.7 mmol) of **7** with 110 ml of 0.05 *M* methanolic base solution (0.52 g of phenol and 0.13 g of sodium, 5.5 mmol each) gave 0.46 g (93%) of crude products which were identified by ir, nmr, and vpc peak enhancement as methyl ester **10** (21%) and methoxy ketone **11** (79%). No phenyl ester of phenoxy ketones were present.[34] Isomer **8** gave an identical result.

Reaction of 1-Chloro-1-phenylbutan-2-one (7) with 0.05 *M* Base and 0.50 *M* Phenol in Methanol. The reaction of 0.50 g (2.7 mmol) of **7** with 110 ml of methanol containing 0.13 g (5.5 g-atom) of sodium and 5.20 g (55 mmol) of phenol gave 0.49 g (94%) of crude products which were identified by ir, nmr, and vpc peak enhancement as methoxy ketone **11** (93%) and isomeric phenoxy ketones **15** (6%) and **14** (1%).[34] Isomer **8** gave an identical result.

Reaction of 1-Chloro-1-phenylbutan-2-one (7) with 2 *M* Sodium Phenoxide in Methanol. The reaction of 0.50 g (2.7 mmol) of **7** with 25 ml of a 2.0 *M* base solution gave 0.56 g (96% yield) of crude product which was identified by ir, nmr, and vpc peak enhancement as the following: methoxy ketone **11** (12%); methyl ester **10** (28%); phenoxy ketones **15** (54%) and **14** (6%).[34] Isomer **8** gave **11** (12%), **10** (25%), **15** (54%), **14** (6%), and phenyl 2-methyl-3-phenylpropionate (3%).

Favorskii Rearrangement of 1-Chloro-3-(*m*-tolyl)propan-2-one (16) with 0.05 *M* Sodium Phenoxide in Methanol. The reaction of 0.32 g (1.8 mmol) of **16**[35] with 70 ml of methanolic solution 0.5 *M* in base (3.5 g-atoms of sodium) and 0.50 *M* in phenol was carried out as described above. The 0.19 g of product (60% yield) was analyzed by nmr, ir, and vpc. Two peaks were present, the first representing 84% and the second 16%. From spectroscopic data the major product was identified as methyl β-(*m*-tolyl)propionate: λ_{max}^{film} 5.79 μ (C=O), 8.67 (CO); $\delta_{TMS}^{CCl_4}$ 2.28 (3, $ArCH_3$), 2.67 (t, 2, CH_2Ar, J = 7.0 Hz), 2.89 (t, 2, CH_2CO, J = 6.5 Hz), 3.57 (3, CH_3O), 6.9–7.3 (m, 4, Ar). The minor product was likewise identified as phenyl β-(*m*-tolyl)propionate: λ_{max}^{film} 5.79 μ (C=O), 8.67 (CO); $\delta_{TMS}^{CCl_4}$ 2.28 (3, $ArCH_3$), 2.68 (t, 2, CH_2Ar, J = 7.0 Hz), 2.97 (t, 2, CH_2CO, J = 6.0 Hz), 6.96 (5, Ph), 6.9–7.3 (m, 4, Ar).

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(34) Under these reaction conditions the phenyl ester was found to be converted to the methyl ester, but the phenoxy ketones are stable.

(35) Prepared by Wayne R. Springer.

Kinetics and Mechanism of *vic*-Diol Dehydration. I. The Origin of Epoxide Intermediates in Certain Pinacolic Rearrangements[1]

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Abstract: The acid-catalyzed pinacolic rearrangements of benzopinacol (tetraphenylethylene glycol), 1,2-di-*p*-tolyl-1,2-diphenylethylene glycol, and tetra-*p*-tolylethylene glycol are characterized by the concurrent formation and accumulation of an intermediate which eventually collapses to form the respective pinacolone products, benzopinacolone (triphenylmethyl phenyl ketone), diphenyl-*p*-tolylmethyl *p*-tolyl ketone, and phenyl di-*p*-tolylmethyl-phenyl ketone, and tri-*p*-tolylmethyl *p*-tolyl ketone. Identification of this intermediate as the epoxide, tetraphenylethylene oxide, 1,2-di-*p*-tolyl-1,2-diphenylethylene oxide, and tetra-*p*-tolylethylene oxide, respectively, was accomplished through spectrokinetic analysis and thin layer chromatography and by observing the kinetic behavior of synthetic material. The origin of the epoxide is due to the proximity of the β-hydroxyl group to the reaction center in the glycol dehydration process. Analysis of titrimetric and spectrophotometric rate measurements performed on the glycols and epoxides established the neighboring group reactivity order as OH $\geq$ *p*-tolyl > phenyl. Due consideration to the energetic requirements for the acid-catalyzed epoxide ring opening leads us to propose a carbonium ion mechanism for these reactions.

For many years the study of pinacolic rearrangements was dominated by a preoccupation with the quantitative evaluation of functional group mobilities. Since this approach proved to be fruitful especially under the able guidance of Bachmann,[4–8] Gomberg,[9]

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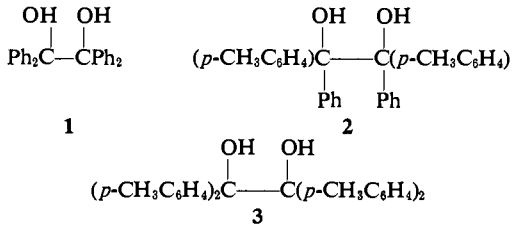
and Bailar,[9,10] the subtler aspects of this reaction received scant attention. Two such aspects are the molecular dynamics of such processes and the question of the intermediates involved in these rearrangements. The scarcity of meaningful kinetic analyses is due in some measure to the fact that the direction of these rearrangements displays a remarkable sensitivity toward such variations as stereochemistry and structure, solvent composition, the nature and strength of the catalyst, and temperature.

In earlier investigations into the rearrangement, the question of intermediates had arisen. Early workers claimed to have dehydrated a number of glycols to the corresponding epoxides without noticing substantial amounts of rearrangement.[11-13] Later these results appeared to be discounted by a kinetic study which purported to prove that the rearrangement of tetrakis(*p*-chlorophenyl)ethylene glycol to its corresponding pinacolone is faster than that of tetrakis(*p*-chlorophenyl)ethylene oxide.[14,15] This analysis remained unchallenged until Gebhart and Adams recognized the intervention of tetraphenylethylene oxide as the intermediate in the rearrangement of benzopinacol as catalyzed by perchloric acid.[16] This state of affairs however does not seem to prevail in aliphatic glycol systems nor in many aromatic substituted glycol systems where in general the epoxides are found to be considerably more reactive than the glycols toward acid catalysts.[17-27]

In this paper we wish to report on our investigation of the kinetics and mechanism of the pinacolic rearrangement of tetraarylethylene glycols and tetraarylethylene oxides. Only *para*-substituted aromatic rings were chosen for inclusion into these substrates because such factors as steric inhibition of resonance, of rearrangement, and of solvation as well as the stereochemical implications of conformational control would be minimized. Intensive study of five substrates clearly indicated that two different but related kinetic schemes were operative. One scheme, applicable to three substrates, is characterized by the formation, accumulation, and destruction of an epoxide intermediate, while the other scheme, applicable to two substrates, does not necessitate the inclusion of this feature. To facilitate the discussion, these substrates and their kinetic descriptions are treated separately. The substrates **1**, **2**, and **3** described in the present paper belong to the class



of compounds whose dehydration is characterized, *inter alia*, by the kinetic description of intermediate accumulation and destruction under rearrangement conditions.

Experimental Section

Materials. The three glycols, **1**, **2**, and **3**, were synthesized by photocoupling the appropriate benzophenones in isopropyl alcohol with a Hanovia uv lamp.[28] Each was recrystallized from benzene–petroleum ether (bp 30–60°) until adjudged pure by titrimetric analysis and by thin layer chromatography.[29] Each glycol was rearranged to its corresponding ketone or ketones[30] and these were purified until adjudged pure by uv and thin layer chromatographic analysis. The epoxides corresponding to each glycol were synthesized by epoxidizing the appropriate tetraarylethylene in chloroform with perbenzoic acid.[31] All epoxides were tested for purity by quantitative conversion to the pinacolone and by thin layer chromatographic analysis.[32]

Tetraphenylethylene and tetra-*p*-tolylethylene were synthesized using the same procedure.[33] The appropriate pinacolone was reduced to the alcohol with $LiAlH_4$ in benzene–ether (1:1) using a Soxhlet extractor and without purification was dehydrated to the olefin in acetic acid using a catalytic amount of sulfuric acid or acetyl chloride. The olefin, 1,2-di-*p*-tolyl-1,2-diphenylethylene, was synthesized by converting 4-methylbenzophenone to the dichloride with PCl_5[34] and coupling the dichloride with finely divided copper metal in anhydrous benzene solution.[35,36]

Solvent acetic acid was originally purified by two methods: (a) by the fractional freezing method[37] and (b) by the oxidation method, followed by careful fractional distillation.[38] Both methods yielded dry acetic acid of high purity. Later we noted that certain batches of Baker Reagent acetic acid were sufficiently pure to be used without further purification. In all the above cases, the freezing point was used as an index of purity, and only acid having mp 16.58° or better was used for kinetic studies.

Anhydrous sulfuric acid (100%) was made by the method of Brand[39] and analyzed according to the method of Gold and Tye.[40] Stock solutions of sulfuric acid in acetic acid, H_2SO_4–HOAc, were made and then standardized against 0.100 *N* potassium acid phthal-

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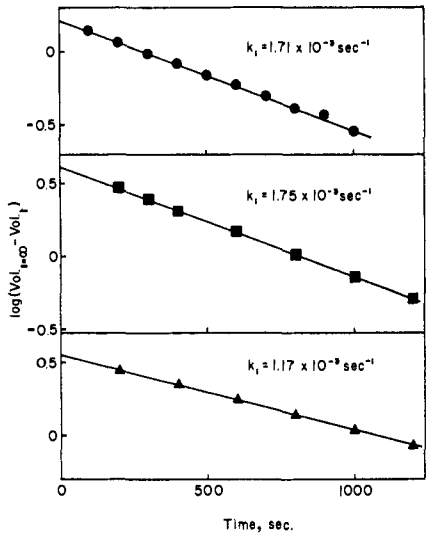

Figure 1. Titrimetric rates of glycol disappearance at 25.0°: ●, benzopinacol in 0.40 M H_2SO_4–HOAc; ■, 1,2-di-*p*-tolyl-1,2-diphenylethylene glycol in 0.10 M H_2SO_4–HOAc; ▲, tetra-*p*-tolylethylene glycol in 0.01 M H_2SO_4–HOAc.

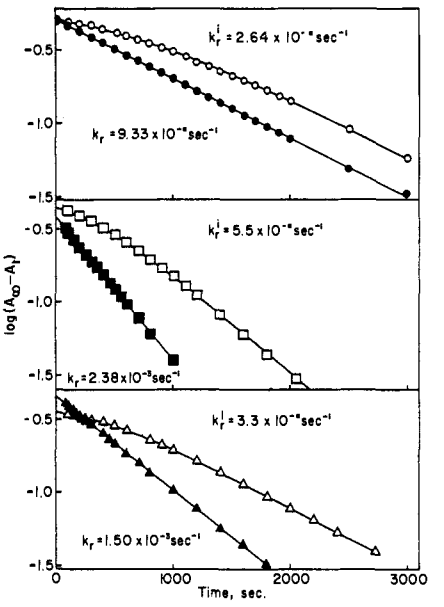

Figure 2. Spectrophotometric appearance of ketone from glycol and epoxide at 25.0°: (upper box) ○, benzopinacol, and ●, tetraphenylethylene oxide, in 0.40 M H_2SO_4–HOAc; (middle box) □, 1,2-di-*p*-tolyl-1,2-diphenylethylene glycol, and ■, 1,2-di-*p*-tolyl-1,2-diphenylethylene oxide, in 0.10 M H_2SO_4–HOAc; (lower box) △, tetra-*p*-tolylethylene glycol, and ▲, tetra-*p*-tolylethylene oxide, in 0.01 M H_2SO_4–HOAc.

ate, KHP, in acetic acid using α-naphtholbenzein indicator. Standard solutions of potassium dichromate, 0.100 N, in water and 0.100 N potassium acid phthalate in acetic acid were made according to contemporary procedures as were 2% starch solutions, 0.10 N sodium thiosulfate, 0.1 N potassium iodide, 1 N sodium acetate, and 0.10 N lead tetraacetate in acetic acid. The sodium thiosulfate was standardized against 0.100 N potassium dichromate.

Kinetic Measurements. Enough glycol was weighed into a 100-ml volumetric flask to make about 10^{-2} M solution. The appropriate amount of acid catalyst from the stock solution was added at time zero. At appropriate intervals aliquots were drawn and quenched in enough KOAc–HOAc to neutralize all the acid catalyst. A measured amount of lead tetraacetate was added such that all the glycol could be oxidized.[41-43] After a 2-hr interval,[44,45a] aliquots of water, KI, and NaOAc solutions were added and the solution was titrated with $Na_2S_2O_3$ to the disappearance of the blue starch end point. Organic precipitate did not obscure the end point. The air oxidation of iodide ion was negligible during the titration. Furthermore, it was independently determined that the corresponding epoxide was not degraded (3% or less) during the analytical procedure employed for glycol determination.

Spectrophotometric rates were run in a Beckman Model D.U. fitted with a specially designed constant-temperature cell compartment. Thermostating was accomplished with a Sargent thermonitor and heater bucking a Forma Temp jr. which circulated cooled liquid through a pipe traversing the bottom of the cell compartment. Continuous agitation of the compartment liquid bath by stirring precluded any but the smallest temperature fluctuations during kinetic measurements. The glycol concentration for these rate studies was around 10^{-5} M.

Each run solution was assayed for acid content by titration against 0.100 N KHP in HOAc. Rate coefficients were obtained graphically.

Thin layer chromatography was performed on glass lantern slides coated with silica gel G. The plates were spotted with a benzene solution of the sample, developed with benzene–heptane (1:1 through 1:3) or heptane–ethyl acetate (1:1 through 3:1) as deemed necessary. Plates were visualized with uv light, $SnCl_4$–$SOCl_2$ vapor, and I_2 vapor.

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Results

In anhydrous acetic acid solvent the rate of benzopinacol dehydration as followed by lead tetraacetate oxidation and iodometric titrimetry over the convenient rate range showed good linear pseudo-first-order kinetics from two to three half-lives, Figure 1. The concentration of sulfuric acid varied from 0.02 to 0.40 M. Under exactly the same conditions (temperature, solvent, and catalyst concentration) the rate of benzopinacolone formation was followed at its λ_{max}, 330mμ, in a Beckman D.U. spectrophotometer. The observed rate coefficient was quite low initially but gradually increased with time until it reached a fairly constant value in the final 25% of reaction, this latter rate coefficient being less than that observed from titrimetric measurements, Figure 2. Since the observed rate coefficient for benzopinacol disappearance differs from that of benzopinacolone appearance, the rate of product formation is less than the rate of substrate dehydration indicating that an intermediate is accumulating. However, since the rearrangement goes to completion, *i.e.*, benzopinacolone accounts for 99 ± 1% of the product, the intermediate must also decompose to give the same product as that obtained from the rearrangement of the glycol.

We have confirmed that the epoxide (tetraphenylethylene oxide) is quantitatively converted to benzopinacolone under acidic conditions. The rate of this latter reaction was studied spectrophotometrically under precisely the same conditions of temperature, solvent, and catalyst concentrations as obtained for benzopinacol. Good linear pseudo-first-order kinetics were obeyed for this rearrangement from three to four half-lives. The quantitative conversion to benzopinacolone was further substantiated by thin layer chromatography, melting point, and uv spectrum of the

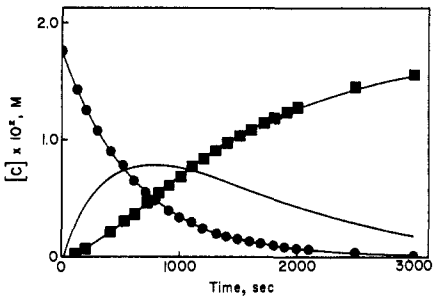


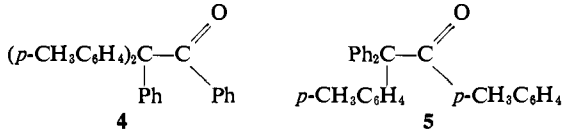
Figure 3. Concentration *vs.* time curves for the components observed in the dehydration of benzopinacol in 0.40 *M* H_2SO_4 at 25.0°: -●-●-●-, benzopinacol; -■-■-■-, benzopinacolone; ———, tetraphenylethylene oxide.

product. Figure 2 illustrates the behavior of the epoxide. The rate of this rearrangement process is slower than the rate of benzopinacol dehydration and thus the epoxide conforms to the basic requirement characterizing the accumulation of an intermediate.

A dynamic picture of the overall process can be observed when aliquots withdrawn at various times from a solution of the glycol undergoing dehydration are quenched and chromatographed on thin layer plates. There are only three components which can be identified within the limits of thin layer chromatographic detection (1% or less), and the fate of each can be followed qualitatively as a function of time. Inasmuch as only three components are present, G, E and K, the concentrations of each of these may be determined quantitatively as a function of time, using the initial molarity of starting glycol, $[G]_0$, and the titrimetric, $[G]_t$, and spectrophotometric rate measurements, $[K]_t$. The material balance allows the concentration of the third component, E, to be computed at any given time, t, so that time–concentration curves for all components become available, Figure 3, Table I.

$$[E]_t = [G]_0 - [G]_t - [K]_t$$

The replacement of hydrogen by a methyl substituent on the aromatic rings of benzopinacol results in an increased reactivity. The substrate 1,2-di-*p*-tolyl-1,2-diphenylethylene glycol dehydrates about 14 times faster than the unsubstituted compound under the same conditions (temperature, solvent, and catalyst concentration). The dehydration followed titrimetrically obeys pseudo-first-order kinetics for 2 to 3 half-lives, Figure 1. The spectrophotometric formation of the two isomeric ketones was observed at the λ_{max}, 325 mμ, of the mixture and the same behavior was found, *i.e.*, increasing rate of ketone production with time until a fairly constant value was observed in the latter 25% of the reaction, Figure 2. The mixture of ketones was found to consist of 92.3% **4** and 7.7% **5** by vapor phase chromatography of the methyl esters de-



rived from the benzoic acids which resulted from base-catalyzed cleavage. This final ratio of the two ketones, **4** and **5**, was found to be essentially identical with the one (**4**:**5** = 12 ± 0.6) measured *during* the acid-catalyzed dehydration of glycol 2, Table II. Here also the disparity in the rates of product appearance and substrate disappearance leads to the conclusion that an

Table I. Components in Benzopinacol Dehydration[a]

Time, sec	$[G]^b \times 10^2$, *M*	$[K]^c \times 10^2$, *M*	$([G] + [K]) \times 10^2$, *M*	$[E]^e \times 10^2$, *M*
0	1.760	0	1.760	0
100	1.490[b]	0.0177	1.508	0.252
120	1.423	0.0284[d]	1.451	0.309
200	1.247	0.0638	1.313	0.447
300	1.064	0.128	1.192	0.568
400	0.901	0.202	1.103	0.657
520	0.766	0.309	1.075	0.685
600	0.652	0.358	1.010	0.750
700	0.544	0.443	0.987	0.773
800	0.467[b]	0.525	0.992	0.768
900	0.386	0.603	0.989	0.771
1000	0.321	0.681	1.002	0.758
1100	0.284	0.752	1.036	0.724
1200	0.240[b]	0.844	1.085	0.676
1300	0.203[b]	0.890	1.093	0.667
1400	0.172[b]	0.957	1.129	0.631
1500	0.146[b]	1.017	1.163	0.597
1600	0.124[b]	1.074	1.198	0.562
1700	0.105[b]	1.127	1.232	0.528
1800	0.093[b]	1.177		
1900	0.078[b]	1.223		
2000	0.065[b]	1.265	1.330	0.430
2100	0.055[b]			
2500	0.028[b]	1.439	1.467	0.293
2520	0.0275[b]			
3000	0.012[b]	1.556	1.568	0.192
3360	0.0069[b]			
3600		1.634		
3800	0.00034[b]	1.654	1.662	0.098
4000	0.00026[b]	1.673	1.676	0.084
∞	0	1.762	1.762	0

[a] In 0.40 *M* H_2SO_4–HOAc as standardized against KHP. [b] Calculated from $[G]_t = [G]_0e^{-k_1t}$ where G = benzopinacol. [c] $[K] = A_{330\ m\mu}/\epsilon_{330\ m\mu}$ where $\epsilon_{330\ m\mu}$ = 280 and K = triphenylmethyl phenyl ketone. [d] Interpolated. [e] E = tetraphenylethylene oxide; $[E] = [G]_0 - ([G] + [K])$.

Table II. Components in 1,2-Di-*p*-tolyl-1,2-diphenylethylene Glycol Dehydration[a] at 25.0°

Time, sec	$[G]^b \times 10^2$, *M*	$[K]^c \times 10^2$, *M*	$([G] + [K]) \times 10^2$, *M*	$[E]^d \times 10^2$, *M*
0	1.265	0	1.265	0
100	1.07	0.030[e]	1.07	0.165
200	0.8915	0.0876	0.978	0.287
300	0.7485	0.187	0.935	0.330
400	0.628	0.293[f]	0.921	0.344
500	0.527	0.399	0.926	0.339
600	0.443	0.496	0.939	0.326
700	0.373	0.589	0.962	0.303
800	0.312	0.675[f]	0.987	0.278
900	0.263	0.755	1.018	0.247
1000	0.223	0.820	1.043	0.222
1100	0.187	0.882	1.069	0.196
1200	0.155	0.931[f]	1.086	0.179
1400	0.1092	1.018	1.127	0.138
1600	0.0769	1.087	1.164	0.101
1800	0.0541	1.136	1.190	0.075

[a] In 0.10 *M* H_2SO_4–HOAc as standardized against KHP. [b] Calculated from $[G]_t = [G]_0e^{-k_1t}$ where G = 1,2-di-*p*-tolyl-1,2-diphenylethylene glycol. [c] $[K] = A_{325\ m\mu}/\epsilon_{325\ m\mu}$ where $\epsilon_{325\ m\mu}$ = 306 and K = phenyl di-*p*-tolylmethylphenyl ketone (**4**) and diphenyl-*p*-tolylmethyl *p*-tolyl ketone (**5**). [d] E = 1,2-di-*p*-tolyl-1,2-diphenylethylene oxide. [e] Extrapolated. [f] Parallel runs carried out on a much larger scale indicate that the ratio of ketones produced during the dehydration of **2** remains essentially constant, [**4**]:[**5**] = 12 ± 0.6.

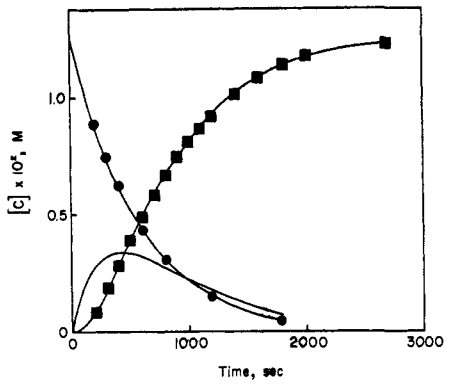


Figure 4. Concentration *vs.* time curves for the components observed in the dehydration of 1,2-di-*p*-tolyl-1,2-diphenylethylene glycol in 0.10 *M* H_2SO_4–HOAc at 25.0°: -●-●-●-, glycol; -■-■-■-, two ketonic products; ——, epoxide.

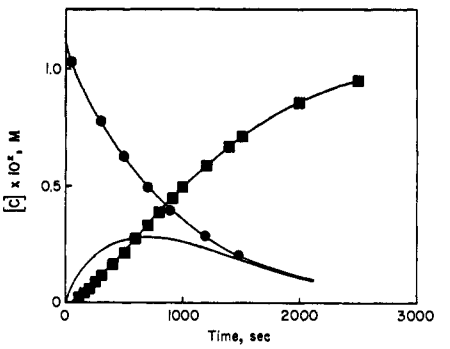


Figure 5. Concentration *vs.* time curves for the components observed in the dehydration of tetra-*p*-tolylethylene glycol in 0.01 *M* H_2SO_4–HOAc at 25.0°: -●-●-●-, glycol; -■-■-■-, ketone; ———, epoxide.

intermediate is accumulating, and thin layer chromatographic analysis indicates that the intermediate decomposes to yield only ketonic products.

The spectrophotometric rate of 1,2-di-*p*-tolyl-1,2-diphenylethylene oxide rearrangement obeyed good linear pseudo-first-order kinetics from 2 to 4 half-lives, Figure 2. Depending upon the acidity, this epoxide was about 33 to 45 times more reactive than the unsubstituted epoxide. Furthermore, the acid-catalyzed rearrangement of 1,2-di-*p*-tolyl-1,2-diphenylethylene oxide leads to a ratio of ketonic products (**4**:**5** = 12 ± 0.6) which is practically identical with the one obtained from the dehydration of glycol **2**. A similar thin layer chromatographic analysis as performed before allowed the rate data to be used in the construction of time–concentration curves for this system, Figure 4, Table II.

Further addition of methyl substituents in the *para* position enhances the reactivity. Tetra-*p*-tolylethylene glycol is about nine times more reactive than the 1,2-di-*p*-tolyl-1,2-diphenylethylene glycol. Essentially the same situation exists here as for the other two substrates.

Table III. Components in Tetra-*p*-tolylethylene Glycol Dehydration[a] at 25.0°

Time, sec	[G][b] × 10^2, *M*	[K][c] × 10^2, *M*	([G] + [K]) × 10^2, *M*	[E][d] × 10^2, *M*
0	1.10	0	1.10	0
100	0.966	0.0188	0.985	0.115
150	0.913	0.0408	0.954	0.146
200	0.863	0.0565	0.919	0.181
250	0.817	0.0816	0.899	0.201
300	0.772	0.107	0.879	0.221
400	0.695	0.159	0.854	0.246
500	0.618	0.214	0.832	0.268
600	0.555	0.268	0.823	0.277
700	0.493	0.325	0.818	0.282
800	0.440	0.386	0.826	0.274
900	0.390	0.440	0.829	0.270
1000	0.354	0.487	0.841	0.259
1200	0.279	0.587	0.866	0.234
1400	0.223	0.669	0.892	0.208
1500	0.201	0.708	0.909	0.191
2000	0.124	0.854	0.978	0.122
2500	0.081	0.944	1.025	0.075

[a] In 0.01 *M* H_2SO_4–HOAc as standardized against KHP. [b] Calculated from $[G]_t = [G]_0e^{-k_1t}$ where G = tetra-*p*-tolylethylene glycol. [c] [K] = $A_{323\ m\mu}$ where $\epsilon_{323\ m\mu}$ = 466 and *K* = tri-*p*-tolylmethyl *p*-tolyl ketone. [d] E = tetra-*p*-tolylethylene oxide.

The glycol shows good pseudo-first-order kinetics for titrimetric oxidative analysis, the linearity ranging from 2 to 3 half-lives, Figure 1. Spectrophotometrically monitored formation of the ketonic product shows the kinetics to be of mixed or complex order with attendant curvature, Figure 2. Thin layer chromatographic analysis indicates three components are present and that the epoxide is an intermediate. Separate spectrophotometric rate studies on the epoxide showed that its behavior is compatible with that expected of an intermediate, Figure 2. Time–concentration curves were also constructed for this system, Figure 5 and Table III.

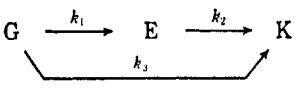
The reactions of these substrates show a strong dependence upon the acidity of the medium. At high acidity both log k_1 and log k_r are linear with $-H_0$, while at low acidities (less than 0.03 *M* H_2SO_4–HOAc) both k_1 and k_r increase linearly with acid concentration, Figures 6 and 7. Added water decreases the reaction rate but does not appear to be a potential nucleophile. This is in accord with the view that water decreases the proton donating capacity of the medium.

Discussion

There are two kinetic schemes which apply to the experimental observations. Both include the formation of the epoxide intermediate, E, from the glycol, G, and its destruction to the ketonic product, K.

Scheme I proposes that the glycol is partitioned

Scheme I



through two different pathways. The ratio $k_1/(k_3 + k_1)$ represents the fraction of glycol which dehydrates to form the epoxide whereas $k_3/(k_3 + k_1)$ represents the fraction which proceeds directly to the ketone. The rate coefficients, k_1 and k_3, may be determined if the concentrations of both E and K can be measured in the initial portion of the reaction before E begins to have a significant rate of decomposition. The rate coefficient k_2 may be extracted from the observed rate coefficient for the decomposition of the epoxide. The pathway, k_3, is necessary to explain the rather large amount of ketone formed in the initial portions of the reaction. Reference to the time concentration curves and the rate coefficients shows that the epoxide concentration is not high enough to account for these large ketone

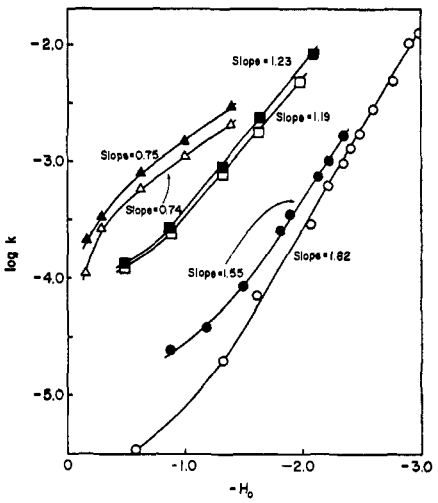


Figure 6. Plot of log k *vs.* $-H_0$[45b] for glycol disappearance and epoxide rearrangement at 25.0°: ○, tetraphenylethylene oxide (slope 1.82); ●, benzopinacol (slope 1.55); □, 1,2-di-*p*-tolyl-1,2-diphenylethylene glycol (slope 1.19); ■, 1,2-di-*p*-tolyl-1,2-diphenylethylene oxide (slope 1.23); △, tetra-*p*-tolylethylene glycol (slope 0.74); ▲, tetra-*p*-tolylethylene oxide (slope 0.75).

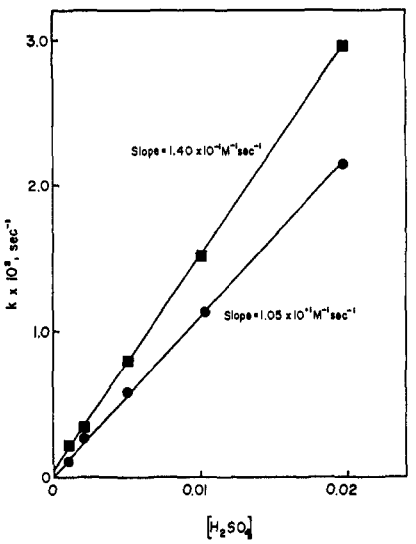
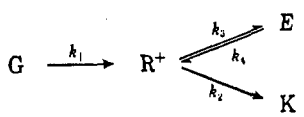


Figure 7. Acidity dependence for glycol disappearance and epoxide rearrangement at 25.0°: ●, tetra-*p*-tolylethylene glycol (slope, 0.140 M^{-1} sec^{-1}); ■, tetra-*p*-tolylethylene oxide (slope, 0.105 M^{-1} sec^{-1}).

concentrations which are generated initially and that an independent path must exist for the conversion of the glycol to the ketone. Scheme I in its formulation implies that a concerted process is involved in each of the conversions.

Scheme II invokes the formation of a carbonium ion

Scheme II



intermediate which may partition to either the epoxide or the ketone. Such a carbonium ion could also attack the solvent to form products resembling the glycol in both structure and kinetic behavior but products of this nature have not been detected on thin layer chromatographic analysis.[46] For Scheme II the rate coefficients, k_1, k_4, and the ratio k_3/k_2 may be evaluated if the concentrations of E and K can be determined in the initial portions of the reaction, *i.e.*, when the decomposition of E does not make a significant contribution to the formation of K. That carbonium ions are actual intermediates in pinacolic rearrangements has been substantiated at least for certain aliphatic pinacols by the work of Pocker, *et al.*,[17-19] and by Stiles, *et al.*[25] Pocker, after applying kinetic and tracer techniques to the rearrangement of pinacol (tetramethylethylene glycol) and after studying some derivatives of pinacol (the appropriate amino alcohol, halohydrin, and epoxide), was led to postulate a carbonium ion intermediate as the only reasonable explanation of the accumulated data.[17-19] Stiles and coworkers used this evidence in a study of migratory aptitudes of alkyl-substituted pinacols but were forced to postulate a hydrated carbonium ion intermediate to explain their data.[25]

(46) Benzopinacol isolated after one half-life of reaction has been found not to have undergone any exchange of its hydroxyl groups with $H_2{}^{18}O$ in dioxane–water mixtures: Sparks and Fry, quoted as personal communication in D. Samuel and B. Silver, *Advan. Phys. Org. Chem.*, 3, 143 (1965).

Similar evidence has accumulated for carbonium ion intermediates in some aryl-substituted glycol systems. Thus Collins, after elegant tracer studies, suggests a carbonium ion intermediate in the rearrangement of triarylethylene glycols.[21-24] Bartlett was led to a similar conclusion after analyzing the rearrangement of 9,10-diphenylacenaphthenediol.[47] More recently evidence for a carbonium ion intermediate in tetraarylethylene glycol rearrangements has accumulated.[48] The outstanding feature shown in Scheme II is that the carbonium ion would be attacked by the neighboring hydroxyl group to form the epoxide which is isomerized to the pinacolone. This type of ring closure is not normally observed in strongly acidic media; furthermore the large amount of strain associated with three-membered rings enhances their reactivity in reaction pathways which release strain. This portion of epoxide chemistry will receive our attention later in this paper. It is because of certain other aspects of epoxide chemistry that we have chosen to present our data in the framework of Scheme II.

In applying Scheme II, it is noted that $-d[G]/dt = k_1[G]$ where k_1 represents the pseudo-first-order rate coefficient for glycol destruction. The rate of epoxide concentration change is given by $d[E]/dt = -k_4[E] + k_3[R^+]$. Assuming that the steady-state approximation is valid here, solving the equation for $[R^+]$ and making the substitution we get

$$\frac{d[E]}{dt} = \frac{k_1[G]}{1 + k_2/k_3} - \frac{k_4[E]}{1 + k_3/k_2}$$

Also

$$\frac{d[K]}{dt} = k_2[R^+]$$

and with appropriate substitutions

$$\frac{d[K]}{dt} = \frac{k_1[G]}{1 + k_3/k_2} + \frac{k_4[E]}{1 + k_3/k_2}$$

(47) P. D. Bartlett and R. F. Brown, *J. Am. Chem. Soc.*, 62, 2927 (1940).

(48) K. Matsumoto, *Bull. Chem. Soc. Japan*, 41, 1356 (1968).

When [G] = 0 the ratio $k_4/(1 + k_3/k_2)$ is identified with the final value k_r. When [E] = 0 the ratio $k_1/(1 + k_3/k_2)$ is identified with the initial value k_r^i.

The partitioning factors k_3/k_2 do not seem to change significantly over the narrow acidity range reported. Those reported for the lowest acidity are to be considered the most reliable because more experimental observations were possible on the initial portions of these slower reactions. As is expected, the factors show that with *para* substitution the aromatic ring seems to compete more favorably with the neighboring hydroxyl group though not as markedly as one might predict, Table IV. However, it must be emphasized

Table IV. Comparison of Partitioning Factors at 25.0°

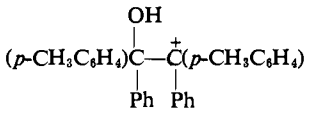
$[H_2SO_4]$, M	$k_r^{ia} \times 10^4$, sec^{-1}	$k_1^b \times 10^3$, sec^{-1}	$k_r^c \times 10^4$, sec^{-1}	k_r^i/k_1	k_r/k_1	$k_r^i/(k_1 - k_r)$
Benzopinacol						
0.40	3.1	1.71	9.74	0.18	0.57	0.22
0.31		1.01	6.19		0.61	
0.16	0.44	0.261	1.45[d]	0.17	0.56	0.21
0.079	0.128	0.799		0.16		0.19
					best value	0.21
1,2-Di-*p*-tolyl-1,2-diphenylethylene glycol						
0.106	5.6	1.76	23.7	0.32	1.35	0.47
0.053	2.15	0.79	9.0	0.27	1.14	0.37
0.02	0.63	0.244	2.66	0.27	1.09	0.35
					best value	0.36
Tetra-*p*-tolylethylene glycol						
0.02	6.6	2.13	29.6	0.31	1.38	0.45
0.01	34	1.12	15.0	0.30	1.34	0.44
0.005	1.75	0.585	7.86	0.30	1.34	0.43
0.002	0.82	0.279	3.40	0.30	1.26	0.43
					best value	0.44

[a] Rate coefficients are derived from the initial portions of the spectrophotometric rate measurements of glycol rearrangement. [b] Rate coefficients from titrimetric rate measurements of glycol dehydration. [c] Rate coefficients from the spectrophotometric rate measurements of epoxide rearrangement. [d] Extrapolated from an acidity dependence plot.

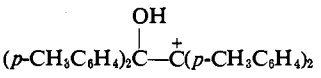
that the overall reactivity of the systems is increasing considerably. Our kinetic analysis and the partition factors were put to a test by asking that they predict both the time in the reaction for achieving the maximum epoxide concentration and that concentration. The results of this test are shown in Table V, and the agreement is good, 10% or less deviation.[49]

The time–concentration curves reveal a kinetically interesting feature apparent only in the latter stages of benzopinacol rearrangement. Here, the epoxide concentration is observed to be much larger than the glycol concentration. The rate of ketone formation then approximates the rearrangement of the pure epoxide. This situation does not exist for the other two substrate systems, for even in the latter stages of glycol rearrangement the glycol and epoxide concentrations are comparable. The rate of ketone formation in these cases, then, cannot approximate that observed for the pure epoxides, Figures 2–5.

Comparisons of reactivity of neighboring groups toward a carbonium ion fall in the order OH $\geq$ *p*-$CH_3C_6H_4$ > Ph. However, the values of the reactivities differ for each substrate in an interesting way. For $Ph_2C(OH)C^+Ph_2$ the reactivity of OH:Ph is 10:1, whereas for

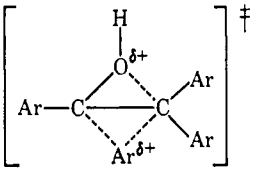


the reactivity of OH:*p*-$CH_3C_6H_4$:Ph is 37:12:1 and for



the reactivity of OH:*p*-$CH_3C_6H_4$ is 54:12. The more stable the carbonium ion becomes, due to substitution, the more discriminating it will be toward neighboring nucleophiles. The apparent nucleophilicity of these neighboring groups should increase with carbonium ion stability, as we have observed.

The chemistry of epoxides is an area which has received considerable attention, and our immediate concern is with reference to epoxide ring opening. A structural rearrangement is the observed consequence of the ring opening process. It is therefore reasonable to ask whether the processes of ring opening and rearrangement occur simultaneously or in a stepwise fashion. A consideration of the topology of the transition state for the concerted ring opening and rearrangement process establishes that there would be significant strain energy involved.



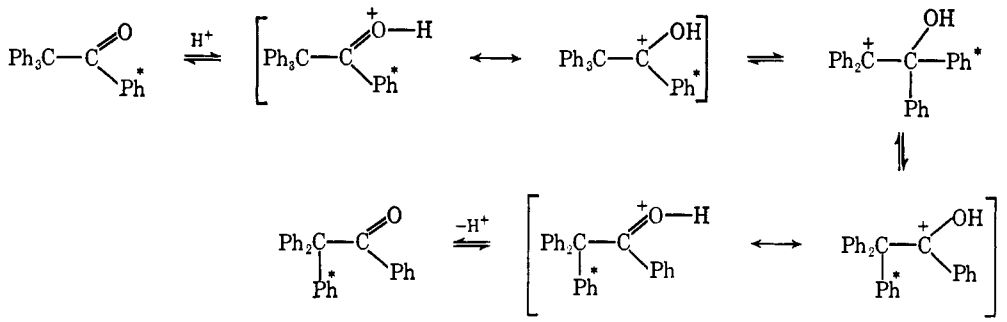
This undesirable transition state strain energy is not operative in the two-step process where ring opening precedes rearrangement, *i.e.*, bond breaking occurs before bond making. The carbonium ion formed immediately after epoxide ring opening but before rearrangement is best represented as a benzhydryl-like cation. The longer the time interval between bond

Table V. Test of Partitioning Factors at 25.0°

$[H_2SO_4]$, M	k_2/k_3	$k_1 \times 10^3$, sec^{-1}	$k_r \times 10^4$, sec^{-1} [a]	$[G]_0 \times 10^2$, M	t_{max},[b] sec	$[E]_{max} \times 10^3$,[c] M
Benzopinacol						
0.40	0.21	1.71	9.74	1.77	780	7.17
					800[d]	7.76[d]
0.16	0.21	0.261	1.45[e]	1.57	5050	6.3
					5050[d]	7.0[d]
1,2-Di-*p*-tolyl-1,2-diphenylethylene glycol						
0.106	0.36	1.76	23.7	1.27	479	2.97
					430[d]	3.45[d]
0.02	0.36	0.244	2.66	1.29	3940	3.34
					3500[d]	3.48[d]
Tetra-*p*-tolylethylene glycol						
0.01	0.44	1.12	15.0	1.13	770	2.65
					700[d]	2.8[d]

[a] $k_r = k_4/(1 + k_3/k_2)$. [b] Calculated from $\ln (k_1/k_r)/(k_1 - k_r) = t_{max}$ (except where noted; see footnote *d*). [c] Calculated from $[E] = k_1[G]_0[e^{-k_1 t} - e^{-k_r t}]/[(1 + k_2/k_3)(k_r - k_1)]$ (except where noted, see footnote *d*). [d] Observed values from time-concentration curves. [e] Extrapolated from an acidity dependence plot.

(49) Scheme I would also predict these same values for $[E]_{max}$ and T_{max}.



breaking and bond making the more clearly defined will be the properties which this ion displays. Thus the ability that this ion displays in distinguishing between the nucleophilicity of various anions or neighboring groups is a most informative property. Furthermore when several neighboring groups are to be distinguished between on this basis their similar entropic advantage causes them to exhibit perhaps a more "intrinsic nucleophilicity."

This carbonium ion should logically also be the same one which is formed from the dehydration of the glycol. Thus from consideration of the epoxide ring opening in the framework of the rearrangement process we were led to discard the concerted mechanism represented by Scheme I. Recently other evidence has been obtained which implicates a carbonium ion in rearrangements of other epoxides.[50]

The only logical explanation for the acid-catalyzed phenyl scrambling in $Ph_3CC(=O)Ph^*$ is that a carbonium ion is formed as an intermediate.[51-53] The mechanism suggested for this process is shown.[53]

The interesting feature about this carbonium ion is that it seems to be immune to attack by solvent molecules. This can be appreciated when all the factors are adequately assessed. First, the lifetime of this ion would be very important in controlling its reaction with potential nucleophiles. For carbonium ions with short lifetimes the nucleophilicity of an attacking reagent is not as pertinent a factor as the proximity effect in directing the course of the reaction. It is to be noted that one of the three neighboring groups is always in an advantageous position to attack when compared to the solvent. If on the other hand the carbonium ion is long lived the nucleophilicity of the attacking reagent governs the course of the reaction often to the virtual exclusion of the proximity effect. Because of the low nucleophilicity of acetic acid containing large amounts of sulfuric acid the neighboring groups may well be potentially more nucleophilic than the medium. Second, the entropic considerations relevant to comparing a bimolecular reaction (collapse with solvent) to a unimolecular reaction (collapse with a neighboring group) favor the latter by a wide margin.[54,55] Third, certain workers have discussed the advantage that neighboring groups display toward a reactive center in terms of their apparently large local "effective" concentration when competing with external nucleophiles.[55] It remains a circumstance that potentially good nucleophiles cannot be observed experimentally to interact with these carbonium ions due to the highly acidic media required to effect both the glycol dehydration and the epoxide ring opening.[56]

(50) K. Matsumoto, *Tetrahedron*, 24, 6851 (1968).
(51) Y. Pocker and B. Ronald, unpublished observations.
(52) The conditions (catalyst, concentration, and temperature) required to bring about phenyl scrambling in $Ph_3CC(=O)Ph$ are quite severe. Since these harsh conditions (8 *M* H_2OS_4–HOAc, 45°) were not required to cause the rearrangement of the glycol or epoxide, the reversibility of the reaction was neglected in our kinetic analysis.
(53) A. Fry, W. L. Carrick, and C. T. Adams, *J. Am. Chem. Soc.*, 80, 4743 (1958).
(54) T. C. Bruice and S. Benkovic, "Bioorganic Mechanisms," Vol. I, W. A. Benjamin, Inc., New York, N. Y., 1966, pp 119-125.
(55) W. P. Jencks, "Catalysis in Chemistry and Enzymology," McGraw-Hill Book Co., Inc., New York, N. Y., 1969, pp 7-30.
(56) Most potential nucleophiles would be rendered ineffective by protonation.