Oxidation of *trans*-Stilbene with Peroxymonophosphoric Acid[1]

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The oxidation of *trans*-stilbene with peroxymonophosphoric acid (H_3PO_5) yielding *trans*-stilbene oxide has been studied in various solvents at 25 °C. The rates in most solvents satisfy the equation: $v = k_2[\text{stilbene}][H_3PO_5]$. The solvents which have strong hydrogen bonding ability decrease the reaction rate. The reaction is catalyzed by H_2SO_4, the rate being correlated with the acidity function H_0, which is not a general phenomenon for the reaction with peroxycarboxylic acid. The reaction carried out in acetonitrile afforded products derived from the further reactions of the epoxide.

Peroxymonophosphoric acid (H_3PO_5) is a strong and effective peracid and can be used as a substitute for peroxycarboxylic acid. We have previously reported on the scope and mechanism for the aromatic hydroxylation,[2] the Baeyer–Villiger reaction of acetophenones,[3] and the oxidation of aromatic amines[4] with H_3PO_5. The present paper is an extension of this study to the H_3PO_5 oxidation of *trans*-stilbene. Generally, it is known that the peroxycarboxylic acid epoxidation is faster in less polar solvents and that there is little or no salt effect and acid catalysis; hence a mechanism involving an attack of peracid activated by intramolecular hydrogen bonding has been accepted.[5] In order to see the possibility of the use of H_3PO_5 for epoxidation of olefins and the characteristic features of the oxidation, we studied the epoxidation of *trans*-stilbene with H_3PO_5 in some solvents and found that *trans*-stilbene oxide was obtained in 73.9% yield in dioxane. The epoxidation was kinetically studied, and the reaction mechanism will be discussed in comparison with that of peroxycarboxylic acid epoxidation.

Results and Discussion

Since H_3PO_4 and H_3PO_5 are both strong acids, the further reaction of generated epoxides may occur. In fact, the reaction of H_3PO_5 with cyclohexene, styrene, and α-methylstyrene gave no isolable epoxides. The oxirane ring of cyclohexene oxide was cleaved by acidic H_3PO_4. Main products from styrene and α-methylstyrene were phenylacetic acid (30%) and 2-phenylpropionic acid (36%), respectively, which were products formed from epoxides via acid-catalyzed alkyl migration.

But on account of the stabilization of the epoxide ring by two phenyl groups, *trans*-stilbene oxide was obtained in a considerable yield. Hence the present study was carried only with *trans*-stilbene.

The reaction of 0.05 molar equiv of *trans*-stilbene with H_3PO_5 was conducted at 25 °C in ethyl acetate, dioxane, ethyl ether, and methanol containing 5% (v/v) acetonitrile in each case. The yields of *trans*-stilbene oxide were as follows: ethyl acetate, 61.0%; dioxane, 73.9%; ethyl ether, 54.4%; methanol, 48.6%. On account of the simultaneously produced H_3PO_4, a secondary reaction of epoxide involving the cleavage of epoxide ring occurred. Therefore, the yields were a little lower than those with peroxycarboxylic acids (with CH_3CO_3H, 78–83%).[6] Since the

Table I. Second-Order Rate Constants for k_2 for the Epoxidation of *trans*-Stilbene with H_3PO_5 at 25 °C and Solvent Parameters

solvent[a]	$10^4 k_2$, $M^{-1} s^{-1}$	γ[b]	DC[c]	DM[d]
ethyl acetate	2.70 ± 0.07	8.4	6.03	1.76
dioxane	2.04 ± 0.05	9.7	2.21	0.4
ethyl ether	1.74 ± 0.07	13.0	4.22	1.17
methanol	1.56 ± 0.08	18.7	32.6	1.69

[a] Each solvent contains 5% (v/v) acetonitrile. [b] Hydrogen bonding parameter. [c] Dielectric constant. [d] Dipole moment. These parameter values were cited from T. Asahara, M. Senoo, and T. Arai, "Yohbai Kohka", Sangyo Tosho, Tokyo, Japan, 1970.

Scheme I
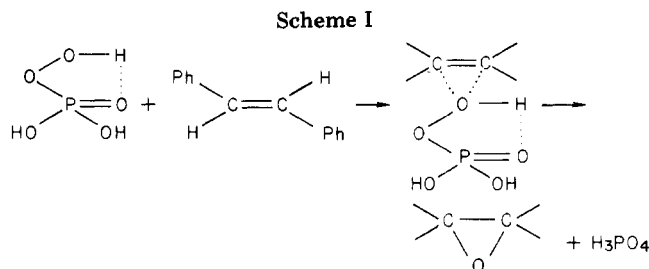
decreases of concentrations of H_3PO_5 and *trans*-stilbene were almost equivalent, H_3PO_5 should not participate in the secondary reaction. The reaction rate is first order in olefin and in H_3PO_5 as shown in eq 1.

$$v = k_2[\text{trans-stilbene}][H_3PO_5] \qquad (1)$$

Solvent Effect. The second-order rate constants for the reaction in four solvents (containing 5% (v/v) acetonitrile which was a solvent for preparation of H_3PO_5) at 25 °C and the corresponding solvent parameters are shown in Table I.

The hydrogen bonding parameter (γ) was defined[7] on the basis of the observed shift of the OD absorption band (3.6–4.35 μm) of CH_3OD, which is approximately proportional to the hydrogen bonding ability of the solvent in benzene. An increase of the γ value means an increase of the hydrogen bonding ability of the solvent. The second-order rate constant k_2 correlates with γ rather than with dielectric constant (DC) or dipole moment (DM), which are parameters of the polarity of solvents. This fact suggests that the intermolecular hydrogen bonding between H_3PO_5 and solvent suppresses the electrophilicity of H_3PO_5, thus retarding the electrophilic attack of peroxidic oxygen on olefins. Hence the reaction may proceed as shown in Scheme I, which is analogous to the scheme for peroxycarboxylic acids.

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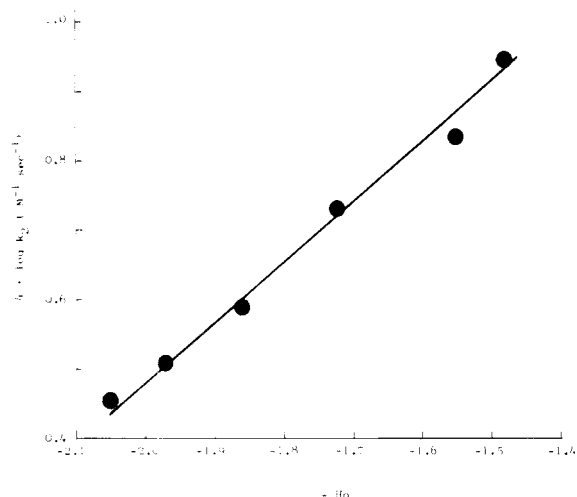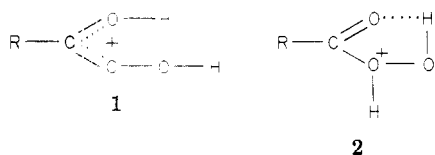
Figure 1. Effect of acidity on the second-order rate constant k_2 at 25 °C in dioxane–acetonitrile (95/5).

As Ogata et al. have reported previously,[3] the Baeyer–Villiger reaction of acetophenones with H_3PO_5 has ca. 100-fold higher rate than that with peroxycarboxylic acid, but this epoxidation with H_3PO_5 shows only a reaction rate comparable to the rate for peroxycarboxylic acids. For example, the second-order rate constant for peroxyacetic acid in dioxane (containing 5% (v/v) acetonitrile) at 25 °C is 1.07×10^{-4} M^{-1} s^{-1}, which is comparable to the k value of 2.04×10^{-4} M^{-1} s^{-1} for H_3PO_5 in the same solvent at 25 °C. The peculiar feature of epoxidation is ascribed to its mechanism; i.e., the intramolecular hydrogen bonding of peracid has little effect on the rate-determining step in the Baeyer–Villiger reaction, while the intramolecular hydrogen bonding has a considerable influence in the epoxidation. And there seems to be little difference between H_3PO_5 and peroxycarboxylic acid in their extent of activation by intramolecular hydrogen bonding.

Effect of Acidity. In general, no acid catalysis is observed in the epoxidation with peroxycarboxylic acid[5] except in the presence of strong acid catalysts such as trichloroacetic acid.[9,10] In the H_3PO_5 epoxidation, an increase of reaction rate was observed with increasing H_2SO_4 concentration. The correlation between rate constant k_2 and acidity function (H_0) of the solution was measured. A plot of log k_2 vs. $-H_0$ gave a straight line with a slope of 0.87 as shown in Figure 1.

It is generally accepted that a straight line for the plot of log k_2 vs. $-H_0$ with a unit slope suggests the participation of a proton at the transition state.[11] In this case, the linear relation of log k_2 vs. $-H_0$ with a slope of 0.87 indicates the participation of a proton in the transition state. The attacking species in the acid-catalyzed epoxidation with peroxycarboxylic acids in the presence of strong acids were assumed to be 1^9 or $2.^{10}$
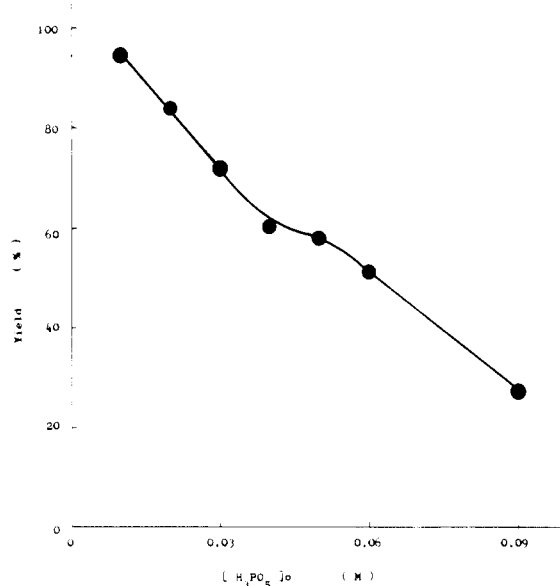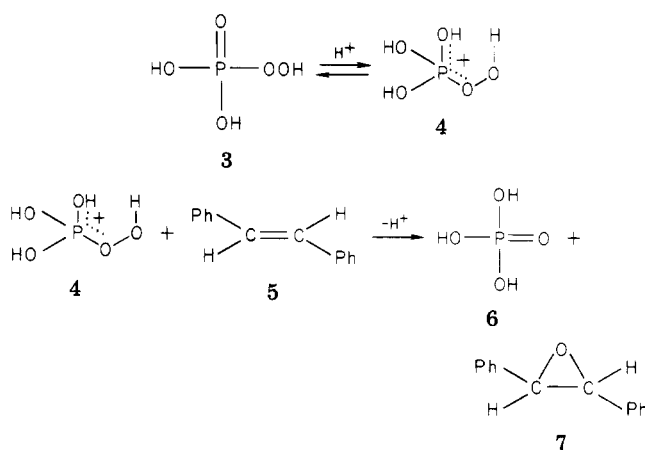

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Scheme II

Figure 2. Effect of $[H_3PO_5]_0$ on yield of *trans*-stilbene oxide at 25 °C in dioxane–acetonitrile (95/5); $[trans$-stilbene$]_0$ = 0.03 M.

H_3PO_5 has structure **3**, and the bond P=O is a p_π–d_π bonding, where the oxygen atom can easily be protonated. Therefore, the acid catalysis may proceed as shown in Scheme II, where the protonation of P=O bonding activates the peracid as an electrophile.

As is apparent from Table I, the reaction proceeds even in the absence of added acid catalysts; in this case, intramolecular activation operates as shown in Scheme I. Therefore, the epoxidation which may proceed via the parallel reaction consisted of uncatalyzed (Scheme I) and acid-catalyzed (Scheme II) pathways.

Effect of Concentration. The yield of *trans*-stilbene oxide decreases with increasing H_3PO_5 concentration as shown in Figure 2. When 0.03 M [*trans*-stilbene]$_0$ is used, the yield is 92–70% at $[H_3PO_5]_0$ < 0.03 M, while at $[H_3PO_5]_0$ > 2[*trans*-stilbene]$_0$ the yield shows a marked decrease, where []$_0$ means initial concentration. Therefore, the good yield is obtained only when excess *trans*-stilbene is used with H_3PO_5.

These results are probably ascribed to the further reaction of the epoxide formed. The further reaction does not lead to stilbene glycol on the basis of NMR spectra of the product mixture; also the products via rearrangement were not detected by GLC. A probable byproduct which causes the decrease of yield under these conditions may be hydroxy alkyl phosphate produced as follows on

the basis of LC peak in comparison with that of the product from the reaction of *trans*-stilbene oxide with H_3PO_4.

$$7 \quad + \quad H_3PO_4 \longrightarrow \quad 8 \qquad (2)$$
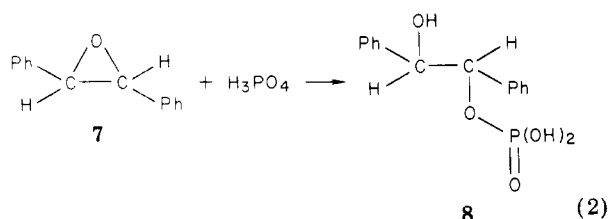
Oxidation in Acetonitrile. When the reaction was carried out in acetonitrile, which is a considerably basic solvent, the further reactions of epoxide involving rearrangement, cleavage, and solvent participation were observed. The products and yields were *N*-diphenylmethylacetamide (**9**) (46.0%), diphenylacetic acid (**10**) (14.0%), 2-methyl-4,5-diphenyloxazoline (**11**) (12.2%), benzaldehyde (**12**) (5.3%), deoxybenzoin (**13**) (2.0%), and so on as shown in eq 3.

$$\xrightarrow[\text{in CH}_3\text{CN}]{} \text{Ph}_2\text{CHNHCCH}_3 \ + \ \text{Ph}_2\text{CHCO}_2\text{H} \ +$$
$$\mathbf{9} \qquad\qquad \mathbf{10}$$
$$+ \ \text{PhCHO} \ + \ \text{PhCH}_2\text{CPh}$$
$$\mathbf{11} \qquad \mathbf{12} \qquad \mathbf{13} \qquad (3)$$
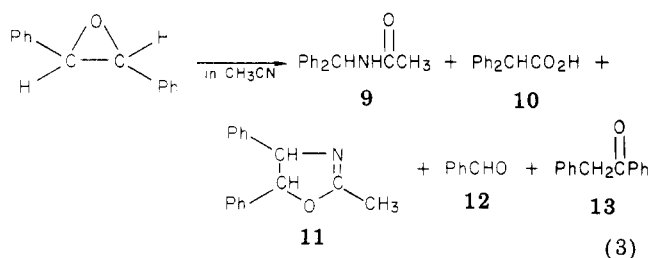
Virtually no *trans*-stilbene oxide remained in the products. Since *trans*-stilbene oxide gives the same products in the reaction with H_3PO_5 in acetonitrile, all of the products should be formed via *trans*-stilbene oxide.

The analogous reactions leading to oxazoline from ethylene oxide and nitriles[12,13] and the reaction leading to **9**[14] have been reported. The observed formation of 2-methyl-4,5-diphenyloxazoline by one step is of interest.

Experimental Section

Materials. *trans*-Stilbene, cyclohexene, styrene, and α-methylstyrene were of guaranteed grade and were used without further purification. Peroxymonophosphoric acid (2–2.5 M) was prepared by the method described in our previous paper.[3] *trans*-Stilbene oxide (mp 68 °C) was prepared by epoxidation of *trans*-stilbene with peroxyacetic acid.[6] *N*-Diphenylmethylacetamide (mp 156 °C) was prepared by the reaction of benzhydrol with acetonitrile.[14] Solvents were purified by distillation as described in the literature.

Products and Rates. Spectra were recorded on apparatuses described below: UV, a Hitachi 124 spectrophotometer; NMR, a Hitachi R-24B NMR spectrometer; GC–MS, a Shimadzu GCMS 7000 gas chromatograph–mass spectrometer (Silicone OV-17, 5% Shimalite W, 2.5 mm × 1.1 m); GLC, a Yanaco G 180 gas chromatograph (Silicone DCQF-1, 5% Chromosorb W, 2.5 mm × 0.75 m; PEG 20 M, 10% Chromosorb WAW, 2.5 mm × 0.75 m); and LC, a Yanagimoto L-1030 liquid-chromatograph (Yanapac DMS column, 2 mm × 0.25 m). Products were identified and estimated by means of GC–MS, GLC, and LC in comparison with those of the authentic samples. Mass spectral data of *N*-(diphenylmethyl)acetamide (**9**) and 2-methyl-4,5-diphenyloxazoline (**11**) were as follows. **9**: 225, 182, 167, 166, 148, 106, 104, **11**: 237, 195, 170, 166, 94, 78. The yields were measured by GLC using diphenyl as an internal standard. The rates were determined mainly by UV spectrophotometry of the remaining *trans*-stilbene (λ_{max} 306 nm, ε 27 200 in methanol) along with the iodometry[15] of remaining H_3PO_5.

Acidity Function.[3,16] The acidity function of dioxane–acetonitrile solvent was measured by means of UV spectrophotometry using *p*-nitroaniline as an indicator and by means of the following equation: $H_0 = \log K_B - \log I$, where $I = (\epsilon_N - \epsilon_A)/(\epsilon_A - \epsilon_S)$. This solvent has log $K_B = 0.651$, $\lambda_N = 358$ nm, and $\epsilon_N = 15\,400$. The H_2SO_4 concentration in N and acidity function (H_0) of the solution were as follows: 0.10 N, 1.48; 0.05 N, 1.55; 0.04 N, 1.72; 0.02 N, 1.86; 0.015 N, 1.97; 0.01 N, 2.05.

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Oxidation of Amines with Sulfonyl Peroxides. 4. The Stieglitz Rearrangement of Tritylamines, Benzhydrylamines, and Benzylamines Induced by *p*-Nitrobenzenesulfonyl Peroxide[1]

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The Stieglitz rearrangement of tritylamines, **2a–g**, benzhydrylamines, **3a–g**, and benzylamines, **4b,c**, is induced by reaction with *p*-nitrobenzenesulfonyl peroxide. Migratory aptitudes for substituted aromatic groups indicate that a concerted cationic aryl migration in the *O*-sulfonylhydroxylamine intermediate obtains. The results are compared with other Stieglitz rearrangements, and they suggest that the charge development on the migrating aryl group is structure and leaving-group dependent.

There are a variety of reactions which involve the migration of an aryl group from carbon to nitrogen.[2a] One

example of such a reaction is the Stieglitz rearrangement of N-substituted amines (eq 1).[2] Of considerable interest