

Dioxirane Chemistry. Part 15.¹ Rate studies on Epoxidations by Dimethyldioxirane²

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The relative rates of epoxidation by dimethyldioxirane, (1), of a series of 4-substituted (*E*)-ethyl cinnamates have been studied. The data were treated with the Hammett linear free energy relationship and give $\rho = -1.53$ indicating an electrophilic O-atom transfer. Second-order rate coefficients were determined for the epoxidation of (*E*)-ethyl cinnamate by (1) at several temperatures and the Arrhenius factors were determined, $E_a = 14.1 \text{ kcal mol}^{-1}\dagger$, $\log (A/s^{-1}) = 7.41$.

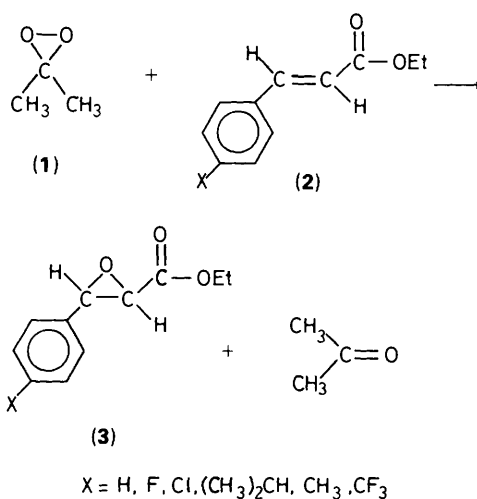
The discovery³ that dimethyldioxirane (1) can be isolated in solution has provided an opportunity for a comprehensive study of the chemistry of this interesting oxidant. The fact that these solutions can be stored at low temperature for several days adds to the facility of using them. To date this experimental approach has been used to study the reaction of (1) with polycyclic aromatic hydrocarbons,⁴⁻⁶ alkenes,^{3,6-10} amines,¹¹⁻¹⁴ sulphides,^{3,15,16} sulfoxides,¹⁵ allenes,¹⁷ aldehydes,³ and saturated hydrocarbons.^{6,18}

The earlier results, as well as those described here, indicate that epoxidations using (1) have substantial advantages over alternative methods. These epoxidations can be carried out at room temperature or below, are high yield, stereospecific processes, and give the epoxide in acetone solution thus permitting easy work-up. In addition the epoxidations are not complicated by the presence of acid or base as is the case with many of the standard methods, and which can be a serious disadvantage when sensitive epoxides are involved. The benefits of the dioxirane method are nicely illustrated by several recent examples. Crandall and Batal¹⁷ have used (1) to convert several allenes into spirodioxides in good to excellent yields. Formation of spirodioxides had been extremely rare since they are usually further transformed under standard epoxidation conditions. Baumstark and co-workers have described^{8,9} the nearly quantitative formation of epoxides from an extensive series of alkenes. We have recently reported⁷ that (1) can be used to convert norbornadiene into the monoepoxide accompanied by very little of the aldehyde rearrangement product which is the major product of alternative methods. By controlling the reaction conditions the *exo,exo* diepoxide of norbornadiene can also be obtained. Use of (1) has permitted Harris and co-workers¹⁰ to synthesize the long-sought 8,9-epoxide of the mycotoxin aflatoxin B.

Our work in dioxirane chemistry is proceeding along two lines, namely (a) demonstrating the synthetic usefulness of the reagent, and (b) carrying out physical organic studies directed at gaining an understanding of the mechanistic details of the reactions of (1) and related dioxiranes.

We earlier reported¹⁵ that use of the Hammett linear free-energy relationship indicated that the oxidation of sulphides and sulfoxides by (1) is an electrophilic process. We were interested in learning whether a similar electronic situation existed in alkene epoxidation by (1).

We describe here the results of a study of the relative rate of epoxidation by (1) in a series of substituted ethyl cinnamates and the application of the Hammett relationship to the results. After this work was completed Baumstark and Jasquez described a similar study⁹ using substituted styrenes and σ^+ values. We also give the results of an absolute rate study in which Arrhenius rate factors were determined.



Scheme.

Results and Discussion

The solutions of (1) in acetone were prepared as previously described.³ The solutions are assayed for dioxirane content by using a GC method and thioanisole which is rapidly and quantitatively oxidized to the corresponding sulfoxide. These solutions were then used to oxidize a series of ethyl cinnamates, (2) (Scheme). The esters were also used to synthesize preparative quantities of the required epoxides (3) for use in GC calibration work.

The competition reactions were carried out by oxidizing an equimolar mixture of (*E*)-ethyl cinnamate and an (*E*)-ethyl 4-X-cinnamate with less than the stoichiometric amount of (1). The reactions were run at 20.5 °C in a constant-temperature bath. The reactions were continued for 1.5 or 2.0 h at which time thioanisole was added to quench any remaining (1). Three separate determinations were made for each substituent and for each reaction time. The relative rate of coefficients (k_X/k_H) were determined from the percentage of esters remaining (Experimental). The logarithms of the relative rates were then plotted against the Hammett σ values. The results (Table 1) for the 1.5 h reaction time gave a ρ value of -1.53 ($r = 0.996$). A similar plot at the 2 h reaction time gave $\rho = -1.45$ ($r = 0.987$). In each case the epoxides are produced with retention of configuration, *i.e.*, each (*E*)-ester gave only the corresponding *trans* epoxide. Edwards and co-workers had earlier shown¹⁹ that (*Z*)- and (*E*)-

† 1 cal = 4.184 J.

cinnamic acids are converted stereospecifically into their respective epoxides using (1) generated *in situ*.

The observed ρ values indicate that dimethyldioxirane is an electrophilic reagent in the epoxidation reaction. Baumstark and Vasquez have recently reported⁹ that epoxidation of a series of substituted styrenes by (1) is also an electrophilic process with $\rho^+ = -0.90$. When one takes account of the fact that the present study used σ values whereas the Baumstark and Vasquez work used σ^+ values then the results obtained are quite similar. A summary of reported ρ values for epoxidation using (1) and some related species is given in Table 2. In all cases the reagents used carry out electrophilic O-atom transfer. The observed values suggest that these reagents also have roughly the same sensitivity to substituent effects.

The absolute rate studies were performed under pseudo-first-order conditions using an excess of (1). The concentrations of (1) used were determined using thioanisole as described above. (*E*)-Ethyl cinnamate was added to a solution of (1) and the resulting solution placed in a constant-temperature bath and stirred. The ratio of (1): ester used varied from 20:1 to 10:1. The consumption of ester with time at each concentration of (1) used was determined by GC with correction of peak areas for response factors (Experimental). Plots of $\log \{[\text{alkene}]_0/[\text{alkene}]_t\}$ versus time gave straight lines from which the values of k_{obs} were extracted. The rate coefficients, k_2 , were obtained from a plot of k_{obs} versus concentration of (1). This procedure was used to obtain values of k_2 at 10, 15, 20, 25, and 30 °C (Table 3). A minimum of four different concentrations of (1) was used at each temperature. A plot of k_2 values versus reciprocal temperature showed Arrhenius temperature dependence of the rate. The epoxidation reaction was found to have $E_a = 14.1 \pm 0.4 \text{ kcal mol}^{-1}$ and $\log(A/s^{-1}) = 7.41$. Baumstark and co-workers have reported^{8,9} second-order rate coefficients for some alkene epoxidations by (1). In all but one case the rate coefficients they report are higher than those measured here for (*E*)-ethyl cinnamate. The lower reactivity of the cinnamate toward (1) is consistent with the electrophilic nature of (1). The lowest rate coefficient measured by Baumstark and Vasquez was that for (*E*)-di-(*t*-butyl)ethylene at $2.4 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ which is to be compared with that of $2.87 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-2} \text{ s}^{-1}$ for (*E*)-ethyl cinnamate at 10 °C. Baumstark and McCloskey have shown⁸ that (*Z*)-alkenes are more reactive than their

(*E*)-counterparts. They have proposed that a spiro transition state for epoxidation could explain these rate differences. Such a transition state would permit a less hindered approach of (1) to the (*Z*)-alkenes. In the case of (*E*)-di-(*t*-butyl)ethylene this steric problem reduces its reactivity to that of the electron-deficient (*E*)-ethyl cinnamate.

The values for the Arrhenius parameters obtained here for (*E*)-ethyl cinnamate can be compared to those which can be extracted from the data of Lynch and Pausacker²⁰ for the epoxidation of 4-substituted stilbenes by perbenzoic acid. For the epoxidation of 4,4-dimethoxystilbene, for example, their data give $E_a = 14.6 \text{ kcal mol}^{-1}$ and $\log(A/s^{-1}) = 8.62$. The lower $\log A$ measured for the epoxidation by (1) indicates a greater negative entropy requirement. The symmetrical transition state for peracid epoxidation suggested by Bartlett²¹ would seem to be somewhat comparable in entropy requirement to the spiro transition state suggested by Baumstark for epoxidation by (1). Further work is required in order better to compare epoxidations by (1) and peracids, however.

Experimental

Instrumentation.—¹H NMR spectra were recorded with either an XL300 or T-60 spectrometer. ¹³C NMR spectra were recorded on the XL300 spectrometer. Deuteriated chloroform, acetone, toluene, and Freon-12 (Aldrich) were used as solvents. All chemical shifts are reported relative to internal SiMe₄ at 0.00 ppm.

Gas chromatography was performed on a Sigma 2000 gas chromatograph interfaced with either a model 3390A or model CR3A Chromatopac integrator. Qualitative and preparative GC work was also performed on a model 700 preparative GC.

Kinetic data were obtained using a constant-temperature bath equipped with a Model 1266-00 immersion circulator.

Materials.—Acetone (Aldrich, reagent grade) was distilled from anhydrous potassium carbonate prior to use. Hexane, ethyl acetate, methylene chloride, and absolute ethanol (US Industrial Chemicals Co.) were used as received.

Oxone (2KHSO₅·KHSO₄·K₂SO₄, DuPont), was obtained from Aldrich and used without further treatment. Thioanisole, methyl phenyl sulphoxide, (*E*)-4-fluorocinnamic acid, (*E*)-4-chlorocinnamic acid, (*E*)-4-trifluoromethylcinnamic acid, *m*-chloroperbenzoic acid, (all obtained from Aldrich), and (*E*)-4-isopropylcinnamic acid (Pfaltz & Bauer) were used as received. (*E*)-Ethyl cinnamate (Eastman) was distilled *in vacuo*, and the purity verified by GLC and NMR data.

Chromatography.—Gas chromatography on the Sigma 2000 was accomplished using a J & W Scientific, Inc. DB-210 capillary column (15 m × 0.25 mm, liquid phase 0.0005 mm), or with a 3% OV-17 on Chromosorb W-HP (80–100 mesh, 4 ft × $\frac{1}{8}$ in) column.

Dry flash chromatography was performed according to a

Table 1. Epoxidation competition reaction of (1) with (*E*)-ethyl 4-*X*-cinnamate vs. (*E*)-ethyl cinnamate.^a

X	$\log k_X/k_H$	σ^b
CH ₃	+0.238	-0.170
(CH ₃) ₂ CH	+0.316	-0.151
F	-0.086	+0.062
Cl	-0.302	+0.227
CF ₃	-0.828	+0.551

^a Reaction time = 1.5 h, Temp. = 20.5 °C. ^b Taken from reference 26.

Table 2. Summary of ρ -values for epoxidation reactions.

Reaction	O-Atom donor	ρ -Value (T/°C, solvent)	Ref.
4- <i>X</i> -Ph-HC=CHCO ₂ Et → epoxide	(1)	-1.53 (20.5, Acetone)	This work
Naphthalene → 1- + 2-naphthols ^a	(4- <i>X</i> -Ph) ₂ C-O-O	+0.93 (0.5, CH ₃ CN)	<i>b</i>
4- <i>X</i> -styrene → epoxide	(1)	-0.90 ^c (23, Acetone)	9
4- <i>X</i> -Ph-HC=CH-Ph → epoxide	PhCO ₃ H	-1.2 (30, benzene)	20
Ph-HC=CH-Ph → epoxide	4- <i>X</i> -PhCO ₃ H	+1.4 (30, benzene)	20
Cyclohexene → epoxide	4- <i>X</i> -PhCO ₃ H	+0.94 (25, xylene)	<i>d</i>
4- <i>X</i> -styrene → epoxide	CH ₃ CO ₃ H	-1.18 ^c , -1.56 (25, acetic acid)	<i>e</i>

^a Reaction is believed to proceed through an arene oxide. ^b S. K. Agarwal and R. W. Murray, *Photochem. Photobiol.*, 1982, **35**, 31. ^c Value for ρ^+ .

^d S. Medvedev and O. Blokh, *J. Phys. Chem. (USSR)*, 1933, **4**, 721. ^e Von B. Fullbier, M. Hampel, and W. Pritzkow, *J. Prakt. Chem.*, 1977, **319**, 693.

Table 3. Second-order rate coefficients for the epoxidation of ethyl cinnamate by (1).

T/K	10 ³ K/T	k ₂ /10 ⁻⁴ dm ³ mol ⁻¹ s ⁻¹	log k ₂
283	3.53	2.87	-3.54
288	3.47	6.01	-3.22
293	3.41	6.88	-3.162
298	3.36	9.08	-3.042
303	3.30	17.90	-2.75

$$E_a = 14.1 \pm 0.4 \text{ kcal mol}^{-1}; A = 1.59 \times 10^7 \text{ s}^{-1}; r = -0.973.$$

modified procedure of Harwood²² using Kieselgel 60 (230–400 mesh ASTM, P. J. Cobert & Assoc.). Thin-layer chromatography was accomplished on Eastman Chromagram silica sheets or Analtech silica uniplates (20 × 20 cm, 250 micron). Chromatographic separations on the Chromatotron Model 7942T (Harrison Research) were accomplished using 1 mm Kieselgel 60 PF₂₅₄ gypsum plates.

General Procedure for the Preparation of Dimethyldioxirane (1).—A 500 cm³ three-necked round-bottom flask containing a mixture of water (40 cm³), acetone (24 cm³, 0.326 mol), sodium hydrogencarbonate (48 g), and a magnetic stirring bar was equipped with a solid addition flask containing peroxy-monosulphate (Oxone, 100 g, 0.163 mol KHSO₅) and a pressure-equalized dropping funnel containing a mixture of water (40 cm³) and acetone (28 cm³, 0.382 mol). An air condenser, loosely packed with glass wool, was attached to the reaction vessel. The top of the condenser was connected to an acetone–solid CO₂ condenser, and this led to a receiving flask (100 cm³) cooled in an acetone–solid CO₂ bath. The receiving flask was also connected to two cold traps (acetone–solid CO₂). Helium or nitrogen gas was passed through the reaction mixture while solid Oxone was added in small portions with the simultaneous dropwise addition of the acetone–water mixture. The mixture was stirred vigorously at room temperature throughout the reaction. After about 15 min, when all of the reagents were combined, a slight vacuum (*ca.* 25 mmHg) was applied to the reaction assembly. The yellow dimethyldioxirane–acetone solution collected primarily in the receiving flask. The dimethyldioxirane solution was stirred briefly with anhydrous magnesium sulphate, filtered, and stored in the freezer for subsequent use.

Solutions obtained in this manner were assayed for dioxirane content using thioanisole (2 cm³, 0.2000 mmol in acetone, to 1 cm³ DMD solution). GLC analysis was conducted on a DB-210 capillary column with the following program: temperature 1, 100 °C; time 1, 3 min; rate, 20 °C min⁻¹; temperature 2, 180 °C; time 2, 4 min; detector, 200 °C; injector, 200 °C; inlet pressure, 20 psi. Concentrations of (1) were then calculated from the percentage conversion of thioanisole to methyl phenyl sulphoxide. Reaction conditions were such as to suppress sulphone formation by using an excess of sulphide, and GLC examination verified the absence of sulphone. Areas were corrected for detector response factors using a solution of the authentic compounds. The concentrations obtained ranged from 0.05 to 0.12 mol dm⁻³ dimethyldioxirane.

Relative Rate Study of the Epoxidation of Cinnamic Acid Esters

Preparation of (E)-Cinnamic Acid Esters (2).—The ethyl esters of (E)-4-fluorocinnamic acid, (E)-4-chlorocinnamic acid, (E)-4-isopropylcinnamic acid, (E)-4-trifluoromethylcinnamic acid, and (E)-4-methylcinnamic acid were prepared by Fischer esterification²³ in absolute ethanol. Purity was verified by TLC, GLC, and ¹H NMR data.

Preparation of epoxides (3) from (E)-Cinnamic Acid Esters.—
(a) *trans*-Ethyl 3-phenyloxirane-2-carboxylate. A freshly prepared solution of (1) (60 cm³, 0.050 mol dm⁻³, 3.0 mmol) was added to a solution of (E)-ethyl cinnamate (0.493 g, 2.80 mmol) in acetone (10 cm³), and stirred at room temperature. The progress of the reaction was determined by GLC. After 3 h, the conversion of alkene into the corresponding epoxide was 23%. The solution apparently no longer contained (1) (as verified by the KI/starch reaction). The solvent was removed by rotary evaporation (10–100 mmHg), and fresh (1) was added. This procedure was repeated until 75% conversion was achieved. The epoxide was separated from ethyl cinnamate using dry flash chromatography with Kieselgel (30 g). Fractions (25 × 20 cm³) were collected using 0–30% ethyl acetate in hexane. Fractions 15–20 afforded the title compound (0.287 g, 71% isolated yield). δ(CDCl₃) 1.25 (3 H, t, *J* 7 Hz), 3.45 (1 H, d, *J* 2 Hz), 4.10 (1 H, d, *J* 2 Hz), 4.25 (2 H, q, *J* 7 Hz), and 7.25 (5 H, s). The coupling constants of the methine protons are consistent with previously reported data for this compound (*J* 1.8 Hz).²⁴

(b) *trans*-Ethyl 3-(4-fluorophenyl)oxirane-2-carboxylate. Ethyl (E)-4-fluorocinnamate (0.427 g, 2.22 mmol) was combined with *m*-chloroperbenzoic acid (0.433 g, 2.51 mmol) in methylene chloride (10 cm³). The solution was refluxed for 4 h, and extracted with 5% NaHCO₃ (3 × 10 cm³) followed by a brine wash. The combined extracts were dried over anhydrous MgSO₄. The solvent was removed by rotary evaporation (10–100 mmHg) affording a pale yellow liquid. GLC analysis indicated 50% conversion of the alkene into the epoxide. The reaction mixture was redissolved in methylene chloride (10 cm³) and fresh *m*-chloroperbenzoic acid (0.259 g, 1.51 mmol) was added. The solution was refluxed for 60 min. Subsequent extraction and removal of solvent showed 80% conversion into the epoxide by GLC analysis. The epoxide was separated from the alkene and acid–peracid mixture by dry flash chromatography on Kieselgel (30 g). Fractions (30 × 20 cm³) using 0–25% ethyl acetate in hexane were collected. Fractions 1–10 afforded the title compound (0.1392 g, 38% isolated yield). δ(CDCl₃) 1.30 (3 H, t, *J* 7 Hz), 3.45 (1 H, d, *J* 2 Hz), 4.10 (1 H, d, *J* 2 Hz), 4.30 (2 H, q, *J* 7 Hz), and 6.8–7.40 (4 H, m).

(c) *trans*-Ethyl 3-(4-chlorophenyl)oxirane-2-carboxylate. The preparation using (1) proved to be much cleaner and was used for all subsequent epoxide preparations. The same procedure as (a) provided *trans*-ethyl 3-(4-chlorophenyl)oxirane-2-carboxylate (55% isolated yield). δ(CDCl₃) 1.28 (3 H, t, *J* 7 Hz), 3.45 (1 H, d, *J* 2 Hz), 4.10 (1 H, d, *J* 2 Hz), 4.30 (2 H, q, *J* 7 Hz), and 7.24 (4 H, s).

(d) *trans*-Ethyl 3-(4-isopropylphenyl)oxirane-2-carboxylate. The same procedure as in (a) provided the epoxide (52% isolated yield). δ(CDCl₃) 1.25 (6 H, d, *J* 7 Hz), 1.25 (3 H, t, *J* 7 Hz), 2.85 (1 H, septet, *J* 7 Hz), 4.20 (2 H, q, *J* 7 Hz), and 7.15 (4 H, s).

(e) *trans*-Ethyl 3-(4-methylphenyl)oxirane-2-carboxylate. The same procedure as in (a) provided the epoxide (42% isolated yield). The epoxide was characterized by ¹H NMR: δ(CDCl₃) 1.35 (3 H, t, *J* 7 Hz), 2.32 (3 H, s), 3.47 (1 H, d, *J* 2 Hz), 4.07 (1 H, d, *J* 2 Hz), 4.28 (2 H, q, *J* 7 Hz), 7.15 (4 H, s).

(f) *trans*-Ethyl 3-(4-trifluoromethylphenyl)oxirane-2-carboxylate. The same procedure as in (a) provided the epoxide (43% isolated yield). The epoxide was characterized by ¹H NMR: δ(CDCl₃) 1.35 (3 H, t, *J* 7.1 Hz), 3.49 (1 H, d, *J* 1.6 Hz), 4.15 (1 H, d, *J* 1.6 Hz), 4.30 (2 H, m), 7.42 (2 H, d, *J* 8.1 Hz), 7.65 (2 H, d, *J* 8.1 Hz), and ¹³C NMR: δ(CDCl₃) 167.64, 139.07, 131.13 (q, ²J_{C-F} 32.7 Hz), 126.13, 125.65 (q, ³J_{C-F} 3.7 Hz), 123.84 (q, ¹J_{C-F} 272.2 Hz), 62.00, 57.06, 56.86, 14.10. (Found: C, 55.13; H, 4.17. C₁₂H₁₁F₃O₃ requires C, 55.39; H, 4.26%).

Competition Reaction of (E)-Ethyl 4-X-cinnamate and (E)-Ethyl cinnamate with (1).—Typical reaction conditions were as

follows: (*E*)-ethyl cinnamate (2 cm³; 0.2000 mol dm⁻³ in acetone; 0.2000 mmol), (*E*)-ethyl 4-*X*-cinnamate (2 cm³; 0.2000 mol dm⁻³ in acetone; 0.2000 mmol), and (1) (3 cm³, 0.050 mol dm⁻³ in acetone; 0.150 mmol) were combined in a 10 cm³ flask equipped with a magnetic stirring bar and a Teflon cap. The flask was placed in a constant-temperature bath at 20.5 ± 0.5 °C, and the solution was stirred. After 2 h or 1.5 h, thioanisole (1 cm³; 0.200 mol dm⁻³ in acetone; 0.200 mmol) was added in order to quench all remaining (1). The solutions were then analysed by GLC under the following conditions: temperature 1, 140 °C; time 1, 2 min; rate, 10 °C min⁻¹; temperature 2, 200 °C; time 2, 2–10 min; detector, 220 °C; injector, 220 °C. No internal standard was used in the experiment due to the reactivity of common standards (hydrocarbons) with (1). The procedure used was based on the amount of starting material consumed at the conclusion of the kinetic run. The injection volumes were not constant enough to allow one to follow absolute areas for either the epoxide or the alkene. By using the combined areas the percentage of converted alkene was calculated. This value was not sensitive to injection volume. The area of the epoxide was corrected for FID response relative to the corresponding cinnamic acid ester. This response factor was measured using a standard solution of the alkene and the epoxide. The standard epoxides were obtained from the preparative-scale reactions described above. Response ratios were generated from the analysis of these standard solutions as follows:

$$R_x = \frac{\frac{[\text{Area } (E)\text{-ethyl 4-}X\text{-cinnamate}]}{[\text{conc. } (E)\text{-ethyl 4-}X\text{-cinnamate}]}}{\frac{[\text{Area trans-ethyl 3-(4-}X\text{-phenyl)oxirane-2-carboxylate}]}{[\text{conc. trans-ethyl 3-(4-}X\text{-phenyl)oxirane-2-carboxylate}]}}$$

This value was used to adjust the integrated area from the chromatogram for the detector response. The adjusted epoxide area was used to calculate the concentration of the alkene at the end of the reaction.

For each reaction the ratio of rate coefficients was obtained as follows:

$$\frac{k_X}{k_H} = \frac{\log[(\% \text{ unchanged ethyl 4-}X\text{-cinnamate})^{-1}]}{\log[(\% \text{ unchanged ethyl cinnamate})^{-1}]}$$

Plots of $\log[k_X/k_H]$ vs. $\sigma^{25,26}$ were used to generate ρ -values for the 1.5 h and the 2.0 h reactions. A linear least-squares correlation was applied to each plot to generate the correlation coefficients, r . The competition reactions were repeated three times for each substituent.

Absolute Rate Study.—Pseudo-first-order reaction conditions were employed using an excess of (1). Typical conditions were as follows. The concentration of (1) was measured at the beginning of the experiment by determining the extent of conversion of thioanisole to the sulphoxide (as described above). (*E*)-Ethyl cinnamate (8.8–15.8 mg, 0.05–0.09 mmol, 0.010 mol dm⁻³ in acetone) was added to (1) (10 cm³; ca. 0.100 mol dm⁻³ in acetone). Ratios of (1):alkene varied from 20:1 to 10:1. The reaction solution was placed in a constant-temperature bath and stirred. The solutions were analysed by GLC: 3% OV-17 column, TCD, programme-temperature 1, 100 °C; time 1, 1 min; rate 10 °C min⁻¹; temperature 2, 200 °C; time 2, 5–10 min;

injector, 250 °C; detector, 250 °C. Areas were corrected for TCD response factors using a standard solution of authentic alkene and epoxide.

The observed rate coefficient was measured for each reaction by analysing for the concentration of (*E*)-ethyl cinnamate by GLC. At each temperature, the concentration of (1) was varied a minimum of four times. A plot of (1) vs. k_{obs} yielded the true second-order rate coefficient, k_2 , from the slope. This procedure was repeated at 10, 15, 20, 25, and 30 °C.

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