Table I. Addition of *dl* Amines and Alcohols to Reagent **1**

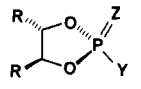
dl compd	^{31}P $\Delta\delta$ (ppm)	integration of low-field diastereomer	integration of high-field diastereomer	α (HPLC)	adduct recovery, %
1-phenylethylamine	0.175	50	50	1.35	99.5
sec-butylamine	0.628	49.6	50.4	1.14	98
1,3-dimethylbutylamine	0.843	48.9	51.1	1.20	97
1-methyl-2-phenoxyethylamine	0.347	50.5	49.5	1.00	100
1-phenyl-1-propanol	0.111	49.5	50.5	1.18	97
2-octanol	0.307	50.1	49.9	1.22	99.5
2-methyl-2-butanol	0.167	50.3	49.7	1.08	96.5
4-methyl-2-pentanol	0.301	49.8	50.2	1.17	97

Table II. Addition of Optically Active Alcohols and Amines to **1**

substrate	% ee by weight	% ee by rotation	% ee by ^{31}P NMR	% ee by HPLC	adduct recovery, %
l-menthol		100	100		96
l-borneol		16.3	16		98.5
(+)-2-octanol	19.7	20	21	20.0	99.5
	49.6	50.1	51	51.5	99.5
	80.3	80.0	81	80.1	99.5
		100	100		97.5
(−)-1-phenyl-ethylamine	32	32	32		98
	48	48	50		99
	70.5	70.5	70.4		99
		95.8	95.7		99

Table I illustrates the technique using a series of racemic amines and alcohols. Table II summarizes data obtained from optically active substrates and compares the ee's determined by weight (dilution of optically pure sample with *dl* sample), by rotation, by ^{31}P NMR,[10] and by HPLC on a silica gel column with hexane/ethyl acetate.

In addition to compounds **1** and **2** shown above, a number of other chiral phosphorus reagents have been examined including the reagents derived from ephedrine but epimeric at phosphorus and the correspsonding reagents derived from pseudo-ephedrine. A number of compounds, **7**, derived from chiral diols, including



7

2,3-butanediol,[11] 1,2-diphenylethanediol, and 1,1′-bi-2-naphthol have been prepared. In this latter series, the phosphorus center is not a chiral unit, and the stereochemistry of the displacement reactions at phosphorus is irrelevant. These reagents tend to be quite reactive. The reagents prepared from 2,3-butanediol and 1,2-diphenylethanediol provided adducts that do not exhibit ^{31}P chemical shift differences comparable to compounds in which the phosphorus atom is chiral, e.g., **3** and **4**;[11] HPLC separations are also less. Side reactions apparently involving ring opening were observed with the use of the reagent (Z = S) prepared from 1,1′-bi-2-naphthol.

Acknowledgment. This work was supported by grant CHE-83 06594 from the National Science Foundation with assistance from the Lubrizol Foundation (fellowship for RCE) and the Monsanto Agricultural Produts Co.

Registry No. 1 (Z = S, Y = Cl), 57651-34-0; **1** (Z = S, Y = (*R*)-1-Phenylethylamino), 91279-05-9; **1** (Z = S, Y = (*S*)-1-phenylethylamino), 66007-24-7; **1** (Z = S, Y = (*R*)-*sec*-butylamino), 91228-05-6; **1** (Z = S, Y = (*S*)-*sec*-butylamino), 91279-06-0; **1** (Z = S, Y = (*R*)-1,3-dimethylbutylamino), 91228-06-7; **1** (Z = S, Y = (*S*)-1,3-dimethylbutylamino), 91279-07-1; **1** (Z = S, Y = (*R*)-1-methyl-2-phenoxyethylamino), 91228-07-8; **1** (Z = S, Y = (*S*)-1-methyl-2-phenoxyethylamino), 91279-08-2; **1** (Z = S, Y = (*R*)-1-phenyl-1-propyloxy), 91228-08-9; **1** (Z = S, Y = (*S*)-1-phenyl-1-propyloxy), 91279-09-3; **1** (Z = S, Y = (*R*)-2-octyloxy), 91237-75-1; **1** (Z = S, Y = (*S*)-2-octyloxy), 91279-88-8; **1** (Z = S, Y = (*R*-3-methyl-2-butanol), 91228-09-0; **1** (Z = S, Y = (*S*-3-methyl-2-butanol), 91279-10-6; **1** (Z = S, Y = (*R*)-4-methyl-2-pentyloxy), 91228-10-3; **1** (Z = S, Y = (*S*)-4-methyl-2-pentyloxy), 91279-11-7; **1** (Z = S, Y = Cl) l-menthol adduct, 91228-11-4; **1** (Z = S, Y = Cl) l-borneol adduct, 91228-12-5; *dl*-1-phenylethylamine, 618-36-0; *dl*-*sec*-butylamine, 33966-50-6; *dl*-1,3-dimethylbutylamine, 54548-48-0; *dl*-1-methyl-2-phenoxyethylamine, 65236-31-9; *dl*-1-phenyl-1-propanol, 613-86-5; *dl*-2-octanol, 4128-31-8; *dl*-3-methyl-2-butanol, 70116-68-6; *dl*-4-methyl-2-pentanol, 20281-88-3; *l*-menthol, 2216-51-5; *l*-borneol, 464-43-7; (+)-2-octanol, 6169-06-8; (−)-1-phenylethylamine, 2627-86-3.

(10) ^{31}P NMR spectra were obtained on a Nicolet NT-300 operating at 121.47 MHz. The spectra were taken in deuterochloroform and reported downfield from external 85% phosphoric acid. The spectra were gated proton decoupled with a delay time of 60 s between pulse sequences (16K data points, 12–20 scans, 90° pulse, 16 μs). Representative chemical shifts: **1** δ 75.90; **2** δ 21.79; derivatives of 1-phenylethylamine and **1** δ 78.51, 78.34; derivatives of 1-phenylethylamine and **2** δ 23.45, 23.42; derivatives of 2-octanol and **1** δ 82.70, 82.39; derivatives of 2-octanol and **2** δ 19.80, 19.76.

(11) After submission of this manuscript a paper appeared that describes the use of **7** (R = Me) as a chiral derivatizing agent for primary and secondary alcohols (Anderson, R. C.; Shapiro, M. J. *J. Org. Chem.* **1984**, *49*, 1304). In accordance with our observations, the authors found **7** to be quite reactive (reaction time with alcohols in the presence of triethylamine and 4-(dimethylamino)pyridine suggested in 15 min). The shift differences found when using **7** are often quite small, e.g., Anderson and Shapiro report that the derivatives of **7** (R = Me) and 2-butanol exhibit $\Delta\delta$ 0.0056 (C_6D_6) whereas the corresponding derivatives of **1** exhibit $\Delta\delta$ 0.200 ($CDCl_3$).

Thianthrene 5-Oxide as Mechanistic Probe in Oxygen-Transfer Reactions: The Case of Carbonyl Oxides vs. Dioxiranes

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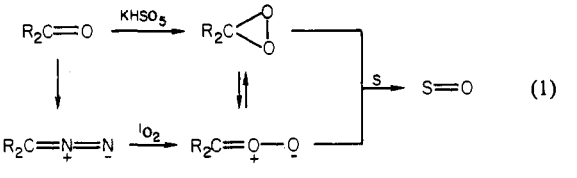
One of the persisting challenging problems concerns the differentiation between carbonyl oxides and dioxiranes (eq 1).[1]



(1)

Despite intensive work, conflicting evidence has accumulated regarding the electrophilic vs. nucleophilic nature of these oxygen-transfer agents. Indeed, the primordial mechanistic question must be raised whether carbonyl oxides and dioxiranes are chemically differentiable species.

The abundant literature[1] reveals that a stringent mechanistic differentiation by employing identical substitution patterns in these

† Undergraduate research participant, spring 1984.

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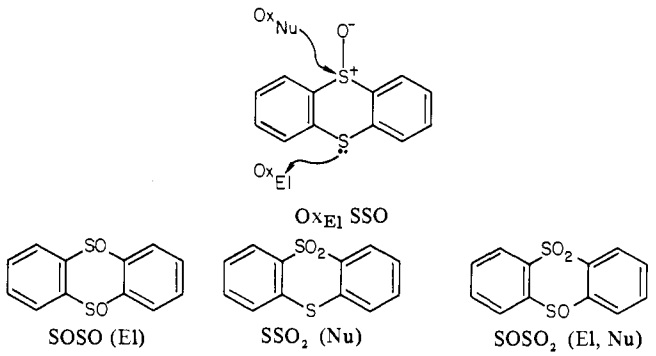
Table I. Nucleophilic Character (X_{Nu}) of Oxygen-Transfer Agents Derived with Thianthrene 5-Oxide

	oxygen-transfer reactions	total yields, %[a]	abs yields, μM[a] SSO_2, n_{Nu}	SOSO, n_{El}	$SOSO_2$, n_{Nu}, n_{El}	X_{Nu}[b]
1.	KO_2; 18-crown-6; C_6H_6; 20 °C	0.50	4.71			1.00
2.	H_2O_2; 1 N NaOH; C_6H_6; 20 °C	0.25	0.886			1.00
3.	*t*-BuOOK; 18-crown-6; C_6H_6; 20 °C	3.65	14.4	0.391		0.97
4.[c]	*t*-BuC(=N_2)Me; $^1O_2$; CH_2Cl_2; −20 °C	0.77	20.0	0.684	0.622	0.96
5.[d]	Et_2S; $^1O_2$; CH_2Cl_2; −20 °C	7.23	53.3	1.55	2.77	0.93
6.[c]	*t*-BuCH=N_2; $^1O_2$; CH_2Cl_2; −20 °C	0.83	41.8	1.63	2.45	0.92
7.[c]	$Ph_2C{=}N_2$; $^1O_2$; CH_2Cl_2; 0 °C	7.76	33.0	0.392	4.24	0.89
8.[e,g]	PhC(=O)C≡CC(=O)Ph; $^1O_2$; CH_2Cl_2	2.92	22.4	3.16	1.82	0.83
9.[e]	PhC(=O)C(=N_2)Ph; $^1O_2$; CH_2Cl_2; 0 °C	6.98	23.7	1.46	6.28	0.80
10.[f]	$Me_2C{=}O$; KSO_5H; 18-crown-6; CH_2Cl_2/H_2O; 0 °C	10.1	75.7	19.3	33.3	0.67
11.[f]	*t*-BuCOMe; KSO_5H; 18-crown-6; CH_2Cl_2/H_2O; 0 °C	5.33	48.0	24.2	6.58	0.64
12.[f]	c-C_6H_{10}(=O); KSO_5H; 18-crown-6; CH_2Cl_2/H_2O; 0 °C	1.88	15.6	8.07	3.15	0.63
13.[f]	*t*-BuCH=O; KSO_5H; 18-crown-6; CH_2Cl_2; H_2O; 0 °C	5.04	42.1	30.3	41.5	0.57
14.	*m*-CPBA; CH_2Cl_2; 20 °C	27.0	22.4	42.7	2.48	0.36
15.[g]	O_3; CH_2Cl_2	3.08	3.86	19.6	0.156	0.17
16.	H_2O_2; 1 N HCl; Et_2O; 20 °C	3.27	0.652	15.0	0.298	0.06

[a] Represents amount of conversion of thiantrene 5-oxide into SSO_2, SOSO, and $SOSO_2$ products, determined by HPLC on a silica gel column, eluting with a 240:10:1 mixture of petroleum ether (64–68 °C)–ethyl acetate–methanol at a flow rate of 3.0 mL/min, using *p*-nitrophenyl sulfone as internal standard; error ca. 3% of stated values; control experiments with $^1O_2$ gave no detectable oxidation products and with KSO_5H ca. 0.1% total yield of oxidation products. [b] Mole fraction of amount of nucleophilic attack, i.e., $n_{Nu}/(n_{Nu} + n_{El})$; $SOSO_2$ represents double oxygen-transfer product either via the sequence SSO $\xrightarrow{Ox_{El}}$ SOSO → $\xrightarrow{Ox_{Nu}}$ $SOSO_2$ or SSO $\xrightarrow{Ox_{Nu}}$ SSO_2 $\xrightarrow{Ox_{El}}$ $SOSO_2$, so that the yield of $SOSO_2$ is equally added to n_{Nu} and to n_{El}. [c] Reference 3a. [d] Reference 8. [e] Reference 7. [f] Reference 2a. [g] The oxidation commenced at −78 °C and was allowed to warm up to 20 °C for HPLC analysis.

agents has so far not been undertaken. Presently we report that thianthrene 5-oxide (SSO), which contains both a nucleophilic



sulfide and an electrophilic sulfoxide site, constitutes a sensitive mechanistic probe for distinguishing between carbonyl oxides and dioxiranes.

Although alkenes, arenes, carbonyl compounds, amines, sulfides, sulfoxides, and phosphines have been extensively utilized as diagnostic tools in oxygen-transfer reactions,[1] in our hands no reproducible and definitive results could be obtained in regard to carbonyl oxides and dioxiranes being distinguishable chemical species. A substrate was essential that would offer in one and the same molecule an electrophilic and a nucleophilic site to the attacking oxidant. Furthermore, the substrate had to be comparatively inert toward the oxidizing reaction conditions under which the oxygen-transfer agents were in situ generated, i.e., Caro's acid ($KHSO_5$)[2] and singlet oxygen ($^1O_2$)[3] (eq 1).

Thianthrene 5-oxide (SSO) has met best the above stringent conditions. Thus, nucleophilic attack at the sulfoxide led primarily to 5,5-dioxide (SSO_2), while electrophilic attack at the sulfide gave predominantly 5,10-dioxide (SOSO).[1a] Unfortunately, both the SSO_2 and SOSO products were further oxidized by the oxygen-transfer agent to 5,5,10-trioxide ($SOSO_2$). The results are summarized in Table I. Control experiments revealed that oxidation of SSO, SSO_2, and SOSO by Caro's acid in the dioxirane generation[2] and by singlet oxygen in the carbonyl oxide production[3] were negligible under the oxygen-transfer conditions.

The chemical behavior of the various oxygen-transfer agents that have been diagnosed by the thianthrene 5-oxide probe range from completely nucleophilic ($X_{Nu} \sim 1.0$) to essentially completely electrophilic ($X_{Nu} \sim 0.06$) in character (Table I). For example, a significant case is hydrogen peroxide, which under basic conditions (Table I, entry 2) acted completely nucleophilically and under acidic conditions (Table I, entry 16) essentially completely electrophilically.[4] As expected, potassium superoxide and potassium *tert*-butyl peroxide gave essentially exclusively nucleophilic attack (Table I, entries 1 and 3).

These two sets of oxygen-transfer reactions convincingly establish that thianthrene 5-oxide differentiates as expected between the nucleophilic and electrophilic nature of the oxidizing species. For comparison also the established[5] electrophilic oxidants *m*-chloroperbenzoic acid (*m*-CPBA) and ozone were tested and as expected gave predominantly electrophilic attack (Table I, entries 14 and 15).

With this mechanistic probe for oxygen-transfer agents on hand, a chemical differentiation between carbonyl oxide and dioxirane was attempted. With the same substitution pattern, i.e., *tert*-butyl and methyl groups, the carbonyl oxide derived from the singlet oxygenation of 2-diazo-3,3-dimethylbutane (Table I, entry 4) as well as the dioxirane derived from the reaction of Caro's acid with pinacolone (Table I, entry 11) revealed themselves as nucleophilic oxygen-transfer agents toward thianthrene 5-oxide. As expected, the carbonyl oxide was appreciably more nucleophilic than *m*-CPBA. The fact that dioxiranes can epoxidize electron-poor substrates[6] better than peroxy acids corroborates the observed nucleophilic order. Also the carbonyl oxide of pivalaldehyde (Table I, entry 6) and the corresponding dioxirane (Table I, entry 13) reveal the same differences in their nucleophilic character as those derived from pinacolone (Table I, entries 4 and 11). Even though a substituent effect was clearly discernable for the carbonyl oxides derived from pinacolone, benzophenone, and benzil (Table I, entries 4, 7, and 9), i.e., the nucleophilic character decreased in the expected order alkyl > aryl > acyl, for all carbonyl oxides

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investigated here, the X_{Nu} values were consistently greater than for all the dioxiranes, i.e., X_{Nu} = 0.80–0.96 vs. X_{Nu} = 0.57–0.67, respectively.

Consequently, thianthrene 5-oxide should serve as diagnostic test for carbonyl oxide vs. dioxirane intermediates in unknown oxygen-transfer reactions by determining the degree of nucleophilic attack (X_{Nu}). For example, oxygen transfer by 2,5-diphenylfuran endoperoxide (Table I, entry 8) appears to involve a carbonyl oxide as intermediate.[7] Similarly, oxygen transfer by the oxidant produced in the singlet oxygenation of alkyl sulfides (Table I, entry 5) is best reconciled in terms of persulfoxide intermediate.[8]

In summary, the present results with thianthrene 5-oxide demonstrate that this probe serves as a useful chemical monitor for differentiating the nucleophilic character of oxygen-transfer agents. In the particular case of carbonyl oxides and dioxiranes, on the basis of the differing degree of nucleophilic attack on SSO, distinct chemical entities are proposed for these oxidants. Although theoretical work[9] designates the dioxirane as the more stable entity by quite a margin ($\Delta E \sim 34$ kcal/mol), the activation barrier for interconversion between these two species is sufficiently high to distinguish them on chemical grounds.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous financial support.

Registry No. SSO, 2362-50-7; SOSO, 951-02-0; SSO_2, 2362-53-0; $SOSO_2$, 2362-54-1; MCPBA, 937-14-4; *t*-BuC(=N_2)CH_3, 65496-01-7; $Na(HO_2)$, 25277-93-4; *t*-BuOOK, 14970-33-3; KO_2, 12030-88-5; $^1O_2$, 7782-44-7; Et_2S, 352-93-2; *t*-BuCH=N_2, 762-64-1; $Ph_2C{=}N_2$, 883-40-9; PC(O)C(=N_2)Ph, 3469-17-8; $Me_2C{=}O$, 67-64-1; *t*-BuC(O)Me, 75-97-8; c-C_6H_{10}(=O), 108-94-1; *t*-BuCHO, 630-19-3; KSO_5H, 10058-23-8; O_3, 10028-15-6; H_2O_2, 7722-84-1; 18-crown-6, 17455-13-9; 2,5-diphenylfuran, 955-83-9.

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Photochemistry on Porous Silica. Correlation of Cage Effects and Magnetic Field Effects with Pore Size

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deMayo and co-workers[1] have published an impressive series of papers dealing with the photochemistry of organic compounds adsorbed on porous silica gel. These authors have convincingly demonstrated that adsorption on silica gel can significantly restrict the translational movement of radical pairs produced by photolysis of adsorbed carbonyl compounds. Results from our laboratory[2] have demonstrated that environments which restrict the translational movement of radical pairs and which encourage recombination of radical pairs are reaction spaces that are suited excellently for the observation of magnetic field and magnetic isotope effects on the chemistry of the radical pairs. Current theory[3] of magnetic field and magnetic isotope effects on the chemistry of radical pairs suggests that both the microviscosity and the size of the reaction space are critical parameters in determining the efficiency of these magnetic effects. We report here a systematic investigation of the influence of pore size, substitute coverage, and applied magnetic field on the photochemistry of ketons adsorbed on porous silica.

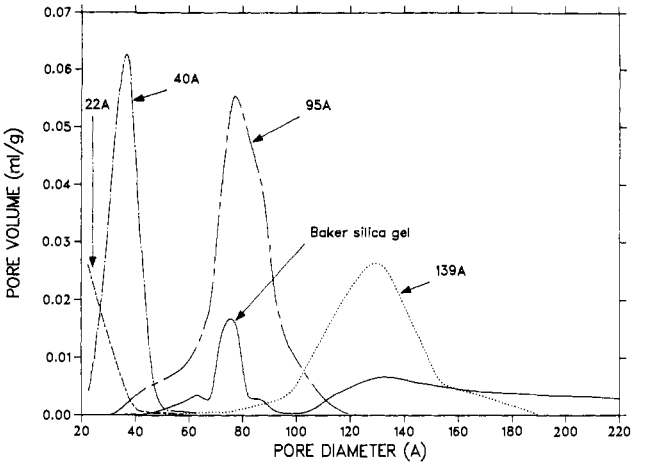
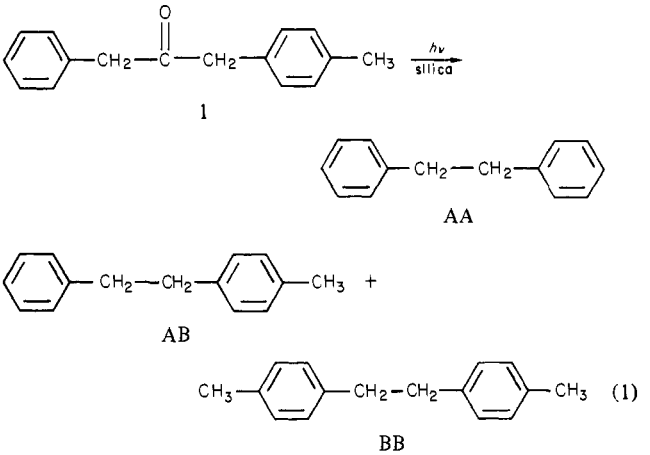


Figure 1. Pore diameter distributions of freeze-formed silicas and Baker silica gel measured by BET. The freeze-formed silicas are designed by their average pore diameters.

3-(4-methylphenyl)-1-phenylacetone (**1**) was deposited on porous silica by adding a calibrated amount of **1** in *n*-pentane to a sample of porus silica soaking in *n*-pentane. The *n*-pentane was evaporated slowly and the resulting sample was placed in a quartz cell equipped with an arm which allowed vacuum degassing (ca. 2×10^{-4} torr). After irradiation of the sample (which was tumbled in order to increase efficiency and reproducibility), CH_2Cl_2 was added to the photolysate which was subjected to GC analysis. In the cases reported, conversions were close to 100%, the cage effects were independent of conversion, the precision was ±5%, mass balances were excellent (>90%), and (unless specified) the only detectable products[4] were those shown in eq 1.



(1)

Since excellent mass balances are obtained, the molar ratio of products (AA, AB, and BB) may be employed to determine via eq 2 the cage effect,[5] i.e., the percent of geminate recombinations

$$\% \text{ cage} = \frac{AB - (AA + BB)}{AA + AB + BB} 100\% \qquad (2)$$

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(4) In the absence of evidence to the contrary, it will be assumed that the conventional mechanism of photolysis of dibenzyl ketone and its derivatives (vide supra, ref 2a) in homogeneous solution and in micellar super cages applies to photolysis of **1** on porous silica.

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