5.9 g, mp 52–56 °C). This on repeated recrystallization from 95% ethanol gave 4.480 g (70% yield, mp 56–58 °C) of white crystals of analytically pure 1-nitro-1-(phenylsulfonyl)propane: ^1H NMR ($CDCl_3$) δ 1.05 (t, 3 H), 2.30 (m, 2 H), 5.50 (AB q, 1 H), 7.80 (m, 5 H); IR (KBr) 6.51 (NO_2), 8.80 μm (SO_2).

Anal. Calcd for $C_9H_{11}NO_4S$: C, 47.16; H, 4.80; N, 6.11; S, 13.98. Found: C, 46.97; H, 4.72; N, 6.30; S, 14.10.

Further acidification of the reaction mixture with 60 mL of ice cold 2.5 N hydrochloric acid, to pH 1, gave 6.7 g of a white solid, mp 72–77 °C; this, presumably, is impure benzenesulfinic acid (mp 83–84 °C).

Preparation of 1-Nitro-1-(phenylsulfonyl)heptane. Under N_2, 0.590 g (0.0148 mol) of sodium hydroxide was dissolved in 8 mL of water, and then 1.015 g (0.007 mol) of 1-nitroheptane and 8 mL of methanol were added; after this was stirred for 30 min, a clear solution was obtained. To this 4.592 g (0.028 mol) of sodium benzenesulfinate in 15 mL of water was added, and then 5.758 g (0.0175 mol) of potassium ferricyanide in 18 mL of water was dropped in over the course of 30 min. After an additional 10 min the reaction flask was cooled in an ice bath, 150 mL of pentane was added, and the mixture was acidified (pH ca. 6) with a cold solution of urea (0.924 g) in 4.7 mL of 20% aqueous acetic acid. The product consisted of a solid phase in addition to the pentane and water phases. The pentane phase was isolated, and the aqueous solid mixture was extracted with four 50-mL portions of pentane, whereupon the solid dissolved. The combined pentane solutions were washed with 30 mL of cold water and then were dried (Na_2SO_4). On removing the pentane, a yellow solid (ca. 1.81 g, mp 44–46 °C) was obtained. This, after repeated recrystallization from pentane, gave 1.483 g (74% yield) of analytically pure 1-nitro-1-(phenylsulfonyl)heptane as white crystals: mp 47–48 °C; ^1H NMR ($CDCl_3$) δ 0.82 (t, 3 H), 1.25 (s, 8 H), 2.25 (m, 2 H), 5.54 (t, 1 H), 7.89 (m, 5 H); IR ($CHCl_3$) 6.51 (NO_2), 8.75 μm (SO_2).

Anal. Calcd for $C_{13}H_{19}NO_4S$: C, 54.73; H, 6.67; N, 4.91; S, 11.22. Found: C, 54.50; H, 6.67; N, 4.80; S, 10.99.

Further acidification of the reaction mixture with a cold solution of urea (1.848 g) in 9.4 mL of 20% aqueous acetic acid to pH 5, followed by pentane extraction, yielded no additional product, nor did further acidification to pH 1 with cold 10% hydrochloric acid, followed by extraction with pentane, give any more product.

Preparation of 1-Nitro-1-(phenylsulfonyl)hexadecane. Under N_2, a 60% oil dispersion of sodium hydride (0.56 g, 0.014 mol) was washed free of oil with pentane, and then 40 mL of *tert*-butyl alcohol was added. After this was stirred for 1 h, 10 mL of water was introduced, and this was followed by 1.897 g (0.007 mol) of 1-nitrohexadecane in 5 mL of *tert*-butyl alcohol. A precipitate formed; after 20 min of stirring 10 mL of water was added, and this gave a clear solution. At this point 4.592 g (0.028 mol) of sodium benzenesulfinate in 65 mL of water was added rapidly, and then 5.758 g (0.0175 mol) of potassium ferricyanide in 19 mL of water was added dropwise over the course of 25 min. Stirring was continued for 10 h, and the product was then acidified (pH 5) by adding a cold solution of 0.924 g of urea in 4.7 mL of 20% aqueous acetic acid over a 5-min period. The resulting mixture was extracted with pentane; the pentane extracts were washed with water and then dried (Na_2SO_4). Removal of the pentane and cooling to 0 °C gave a white solid which on repeated recrystallization from hexane yielded 1.720 g (60%) of pure 1-nitro-1-(phenylsulfonyl)hexadecane: mp 65–66 °C; ^1H NMR ($CDCl_3$) δ 0.8 (t, 3 H), 1.25 (s, 26 H), 2.15 (m, 2 H), 5.50 (t, 1 H), 7.75 (m, 5 H); IR (KBr) 6.50 (NO_2), 8.67 μm (SO_2).

Anal. Calcd for $C_{22}H_{37}NO_4S$: C, 64.24; H, 9.00; N, 3.40; S, 7.79. Found: C, 64.27; H, 9.08; N, 3.42; S, 8.00.

Further acidification of the reaction mixture with 20 mL of ice cold 2.5 N hydrochloric acid, followed by extraction with pentane, gave nothing.

Acknowledgment. We are indebted to the National Science Foundation for support of this work.

Registry No. 1-Nitrooctadecane, 66292-30-6; cyclododecylamine, 1502-03-0; nitrocyclododecane, 1781-70-0; nitrocyclohexane, 1122-60-7; nitrocyclopentane, 2562-38-1; 2-nitrobutane, 600-24-8; potassium ferricyanide, 13746-66-2; sodium nitrite, 7632-00-0; 1,1-dinitrocyclohexane, 4028-15-3; 2,2-dinitrobutane, 5437-66-1; 2,2-dinitrooctane, 84065-75-8; 1,1-dinitrocyclopentane, 10515-17-0; 1,1-dinitrocyclododecane, 84065-76-9; 2-nitrooctane, 4609-91-0; 1-nitroheptane, 693-39-0; 1,1-dinitroheptane, 10229-05-7; 1,1-dinitrodecane, 3759-58-8; 1-nitrodecane, 4609-87-4; 1,1-dinitrooctadecane, 84065-77-0; 2-nitropropane, 79-46-9; 2-nitroheptane, 617-72-1; 2-cyano-2-nitropropane, 18992-13-7; 2-cyano-2-nitrobutane, 84065-78-1; potassium cyanide, 151-50-8; 2-cyano-2-nitroheptane, 84065-79-2; 1-cyano-1-nitrocyclopentane, 84065-80-5; 1-cyano-1-nitrocyclohexane, 58102-55-9; 1-cyano-1-nitrocyclododecane, 84065-81-6; α-nitroisopropyl phenyl sulfone, 41774-06-5; sodium benzenesulfinate, 873-55-2; α-nitrocyclopentyl phenyl sulfone, 41774-10-1; α-nitrocyclohexyl phenyl sulfone, 41774-11-2; α-nitrocyclododecyl phenyl sulfone, 84065-82-7; α-phenylnitroethane, 7214-61-1; 1-nitropropane, 108-03-2; 1-nitro-1-(phenylsulfonyl)-1-phenylethane, 84065-83-8; 1-nitro-1-(phenylsulfonyl)propane, 21272-84-4; 1-nitro-1-(phenylsulfonyl)heptane, 78258-04-5; 1-nitro-1-(phenylsulfonyl)hexadecane, 84065-84-9; 1-nitrohexadecane, 66271-50-9.

Photoepoxidation of Propylene at Elevated Pressures Sensitized by α-Diketones

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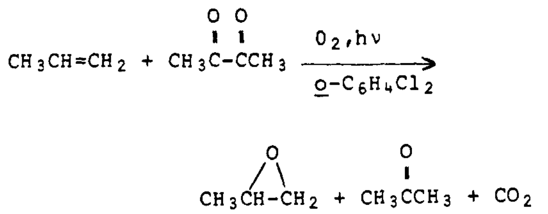
The α-diketone sensitized photooxygenation of saturated propylene solutions (*o*-dichlorobenzene) at atmospheric pressure proceeds with high selectivity to propylene oxide. The effect of changing sensitizer concentration on the rate of epoxidation was determined for biacetyl, 1-phenyl-1,2-propanedione, and benzil. A small enhancement of the rate was achieved by using mixtures of biacetyl and 1-phenyl-1,2-propanedione. Pressurization of the reaction (140–185 psia) allowed the use of greater solution concentrations of propylene and oxygen and resulted in significant rate enhancement. In concentrated propylene solutions (≥3.2 M) the formation of epoxide decreased as oxidative cleavage to acetaldehyde and formaldehyde increased. Total propylene conversion remained relatively constant at these concentrations.

As part of our program to develop novel routes to chemicals of commercial importance, we have been concerned with photochemical oxidations of simple organic compounds. Photooxidations of olefins with molecular oxygen to produce the corresponding epoxides have been of particular interest. Several conversions of this type have been reported. For example, the reaction of sterically hindered alkenes like biadamantylidene and 7,7′-binorbornylidine with photochemically generated singlet oxygen produces the corresponding epoxides in addition to the expected 1,2-dioxetane products.[1-3] Sulfur dioxide has been shown to sensitize photoepoxidation of alkenes, apparently via a charge-transfer process.[4] Under the conditions of this reaction, however, the epoxides react with sulfur dioxide, and polymeric alkylene sulfonates are the major products isolated. Ogata[5] recently described a photoepoxidation sensitized by benzoins and acyloins in which acylperoxy radicals, formed by photooxidative decomposition of the sensitizer, were found to be the active epoxidizing species. In 1976, Bartlett reported a highly efficient photoepoxidation sensitized by α-diketones.[6] Oxidative decomposition of the sensitizer was also observed in this reaction, but it was not stoichiometrically involved in the epoxidation. Mechanisms involving diradical intermediates from which the α-diketones may be regenerated were proposed.[6,7]

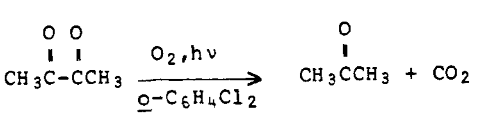
We now report the successful application of the α-diketone-sensitized photooxidation reaction to the epoxidation of propylene (and other gaseous olefins). We also report that the rate of photoepoxidation is enhanced by the use of sensitizer systems composed of two or more α-diketones and by running the reaction under moderate pressures. An interesting oxidative cleavage that occurs at high propylene concentrations is also discussed.

Results and Discussion

Irradiation (450-W high-pressure mercury lamp or 1000-W tungsten filament lamp) of oxygen saturated *o*-dichlorobenzene solutions of propylene (0.38 M, saturated) and biacetyl (0.07–0.16 M) in a cylindrical Pyrex photoapparatus at 15–18 °C for 1–3 h produced propylene oxide in high selectivity (90–95%). The only other products detected by GC were identified (mass spectroscopy) as carbon dioxide and acetone. A control experiment in which propylene was excluded also produced carbon dioxide and acetone, indicating that these are products of sensitizer decomposition rather than propylene oxidation (eq 1).



$$\mathrm{CH_3CH{=}CH_2 + CH_3\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow[\underline{o}\text{-}C_6H_4Cl_2]{O_2,h\nu} CH_3\overset{O}{\overbrace{CH{-}CH_2}} + CH_3\overset{\overset{O}{\|}}{C}CH_3 + CO_2} \qquad (1a)$$



$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow[\underline{o}\text{-}C_6H_4Cl_2]{O_2,h\nu} CH_3\overset{\overset{O}{\|}}{C}CH_3 + CO_2} \qquad (1b)$$

The complete destruction of biacetyl reported by Bartlett[6] was not observed even upon prolonged irradiation (>6 h).

Irradiation of saturated propylene solutions containing benzil or 1-phenyl-1,2-propanedione also resulted in epoxidation. As in the biacetyl-sensitized epoxidations, acetone and carbon dioxide were minor products of reactions sensitized by 1-phenyl-1,2-propanedione. Control experiments indicated that sensitizer photooxidation was again responsible for the formation of the side products (isolation or identification of aromatic decomposition products was not attempted). Reactions sensitized by benzil, which appeared to be completely stable toward photooxidation, produced propylene oxide exclusively. Several other benzil derivatives including 4,4′-dimethylbenzil and 4,4′-dimethoxybenzil also sensitized the photoepoxidation but were not studied in detail.

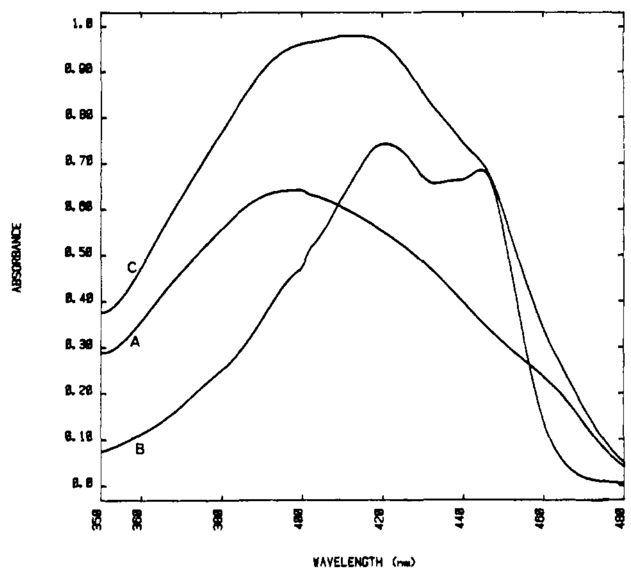


Figure 1. UV–visible spectra in *o*-dichlorobenzene of (A) $\mathrm{PhCOCOCH_3}$ (0.02 M), (B) $\mathrm{CH_3COCOCH_3}$ (0.03 M), and (C) a mixture of $\mathrm{PhCOCOCH_3}$ (0.024 M) and $\mathrm{CH_3COCOCH_3}$ (0.012 M).

For determination of the relationship between the rate of sensitized photoepoxidation and the concentration of the sensitizer, saturated propylene solutions (0.38 M) in *o*-dichlorobenzene containing various quantities of α-diketones were irradiated under identical conditions. After irradiation the solutions were analyzed for propylene oxide by GC. Each reaction was run to low propylene conversion (≤15%) to ensure a uniform epoxidation rate. In separate experiments analysis of reaction mixtures at several intervals (20 min) ensured that the production of propylene oxide was uniform over a 2-h irradiation period.

Epoxidation rates obtained with biacetyl, benzil, and 1-phenyl-1,2-propanedione appear in Table I. In general, rates of photoepoxidation showed approximately a first-order dependence on sensitizer concentration until a maximum was reached. Higher sensitizer concentrations resulted in lower rates. This behavior may be attributed to the light-absorbing properties of the sensitizers. Highly concentrated sensitizer solutions will absorb all usable light in a fraction of the reactor path length nearest the lamp. The high localized concentration of excited states rapidly depletes the oxygen in this region of the reactor, decreasing the overall efficiency of the photoepoxidation. This results in lower observed rates.

The lamps used in these experiments emit light over a wide region of the UV and visible spectrum. A sensitizer with a n–π^* absorption band wider than that of the α-diketones would absorb a greater amount of this available light and might therefore produce a greater quantity of photoproducts. A convenient method of producing sensitizers with a greater bandwidth is to use a mixture of two or more α-diketones with overlapping absorption bands. Inspection of absorption spectra of the available α-diketones suggested that a mixture of 1-phenyl-1,2-propanedione and biacetyl could significantly increase the quantity of light absorbed in a photoepoxidation reaction.

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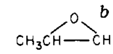
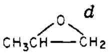
[1] Jefford, C. W.; Boschung, A. E. *Helv. Chim. Acta* **1977**, *60*, 2673.
[2] Bartlett, P. D.; Ho, M. S. *J. Am. Chem. Soc.* **1974**, *96*, 627.
[3] Schaap, A. P.; Faler, G. R. *J. Am. Chem. Soc.* **1973**, *95*, 3381.
[4] Sasaki, T. *J. Am. Chem. Soc.* **1981**, *103*, 3882.
[5] Sawaki, Y.; Ogata, Y. *J. Am. Chem. Soc.* **1981**, *103*, 2049.
[6] Shimizu, N.; Bartlett, P. D. *J. Am. Chem. Soc.* **1976**, *98*, 4193.
[7] Bartlett, P. D.; Becherer, J. *Tetrahedron Lett.* **1978**, 2983.

Table I. Variation of Propylene Epoxidation Rate with Sensitizer Concentration[a]

sensitizer	concn, M	time, H	 [b] mmol	epoxidation rate × 10^2, M h^{-1}
$CH_3COCOCH_3$ [c]	0.07	1.5	3.49	0.93
	0.09	1.5	5.04	1.34
	0.13	3.0	15.00	2.00
	0.16	1.5	4.78	1.28
PhCOCOPh [c]	0.08	2.0	7.00	1.40
	0.10	2.0	10.43	2.09
	0.11	2.0	6.34	1.27
	0.14	2.0	1.47	0.29
$PhCOCOCH_3$ [d]	0.07	1.2	2.84	0.95
	0.10	1.2	4.97	1.66
	0.11	1.2	3.83	1.28
	0.12	1.2	3.52	1.17
	0.14	2.0	4.31	0.86

[a] In 250 mL of *o*-dichlorobenzene saturated with propylene (0.38 M) at 15-18 °C. [b] Determined by quantitative GC. [c] 450-W high-pressure mercury lamp. [d] 1000-W tungsten filament lamp.

Table II. Propylene Photoepoxidations Sensitized by Mixtures of $PhCOCOCH_3$ and $CH_3COCOCH_3$ [a]

sensitizer ratio[b]	concn,[c] M	time, h	 [d] mmol	epoxidation rate × 10^2, M h^{-1}
1:2	0.11	1.2	3.88	1.29
1:1	0.11	1.2	4.91	1.64
2:1	0.11	2.5	11.00	1.76
2:1	0.03	1.2	3.31	1.10
2:1	0.06	1.2	7.09	2.36
2:1	0.07	2.5	16.70	2.67
2:1	0.10	2.5	12.50	2.00
2:1	0.12	2.5	7.97	1.28

[a] In 250 mL of *o*-dichlorobenzene saturated with propylene (0.38 M) at 15-18 °C. Irradiation with a 1000-W tungsten filament lamp. [b] Molar ratio of $PhCOCOCH_3$ to $CH_3COCOCH_3$. [c] Total concentration of α-diketones. [d] Determined by quantitative GC.

A series of propylene photoepoxidations sensitized by 1-phenyl-1,2-propanedione–biacetyl mixtures was run (Table II). Best results were obtained with a 2:1 molar ratio (1-phenyl-1,2-propanedione to biacetyl). The UV-visible absorption spectra of 1-phenyl-1,2-propanedione, biacetyl, and the 2:1 mixture appear in Figure 1. The broad and flat shape of the absorption band of the mixture allows strong absorption of light over a relatively wide range of wavelengths (360–460 nm) with highly uniform absorption from 385 to 430 nm. The variation of epoxidation rate with the concentration of mixed sensitizer was similar to that observed with the individual sensitizers. However, the greater light-absorbing capacity of the sensitizer mixture results in a greater maximum rate reached at a lower sensitizer concentration.

Pressurized Photoepoxidations. The epoxidation rates obtained by bubbling oxygen through saturated propylene solutions are arelatively low, due largely to the limited solution concentrations of the reactants. The saturation concentration of propylene in *o*-dichlorobenzene was measured as 0.38 M. The solubility of oxygen in organic solvents, as determined from Ostwald constants,[8] is between 0.008 and 0.019 M under 1 atm of oxygen. Continuous bubbling of oxygen through the reaction mixture is necessary to maintain this concentration; however, this lowers the effective propylene concentration by stripping it from solution. These problems may be overcome by pressurizing the photoepoxidation system. The pressure in such a gas–liquid system should not effect the rate constant of the photoepoxidation but should increase the reaction rate by raising the concentrations of the dissolved gases.[9] Moderate pressures (≥150 psia) are sufficient to condense propylene and, in combination with vigorous stirring, will maintain the maximum solution concentration of oxygen throughout the reaction.

The pressurized photoepoxidations were run in a pressure reactor consisting of a 750-mL bowl (0.25-in. flint glass) bolted to a stainless steel cover. The reactor was equipped with an internal cooling coil, a thermometer well, and an air-driven propeller stirrer assembly. Irradiation was provided by a 450-W high-pressure mercury lamp in a Pyrex immersion well placed 1.0 cm from the reactor wall. Care was taken to place the lamp exactly in the same position for each run.

The necessity of irradiating the pressure reactor externally through thick glass and the presence of objects inside the reactor (i.e., the propeller and cooling coil) reduced the amount of light reaching the reaction mixture. Comparison of the reaction rates measured in this reactor with those obtained in the cylindrical reactor are not valid. Therefore, a base-case reaction was run on a saturated propylene solution (0.38 M) containing a 2:1 1-phenyl-1,2-propanedione–biacetyl mixture (0.04 M) under 1 atm of oxygen for 1.5 h at 15–22 °C. With use of the same sensitizer composition, solutions of higher propylene concentrations (2.8–12.2 M) were irradiated at elevated pressures (140–180 psia with 15–20 psi of oxygen[10]). The epoxidation rates of these reactions were compared with the rate obtained in the base-case reaction (2.93×10^{-3} M h^{-1}) to establish the effects of increased propylene concentration (Table III).

Photoepoxidations in concentrated propylene solutions under moderate pressures were more rapid than under base-case conditions. In addition, acetone and carbon dioxide formation due to sensitizer photodecomposition was not observed. Epoxidation rates increased with propylene concentrations up to 3.2 M (8.4 times more concentrated than saturation at atmospheric pressure) where a rate 7.5 times greater than the base-case rate was observed. At propylene concentrations >3.2 M the rate of propylene oxide formation began to decline at the expense

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[8] Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973; p 89.

[9] Mirbach, M. F.; Mirbach, M. J.; Saus, A. *Chem. Rev.* 1982, *82*, 59.

[10] For prevention of the formation of potentially explosive gas mixtures, the O_2 partial pressure was limited to 20 psi. Nitrogen was introduced as required to bring the system to operating pressure.

Table III. Pressurized Photooxidations of Propylene[a]

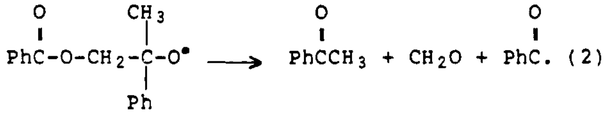
$[CH_3CH{=}CH_2]$, M	P_{tot}, psia	P_{O_2}, psi	$CH_3CH{=}CH_2$ conversion, mmol	$CH_3CH\overset{O}{—}CH_2$ mmol	CH_3CHO,[b] mmol	rel epoxidation rate[c]	selectivity to $CH_3CH\overset{O}{—}CH_2$[d] %
0.38	15	15	1.60	1.60	0	1.0	100
2.81	159	20	8.45	8.45	0	4.9	100
2.95	150	14	8.83	8.83	0	5.4	100
3.20	158	18	12.10	11.24	0.86	7.5	92.9
3.70	170	20	10.49	9.22	1.27	7.3	87.9
6.30	170	20	12.20	7.70	4.50	5.6	63.1
9.60	172	20	11.20	4.87	6.33	3.4	43.5
12.20[e]	185	20	10.20	3.03	7.17	3.0	29.7

[a] In *o*-dichlorobenzene with irradiation by a 450-W high-pressure mercury lamp for 1.5 h. [b] When acetaldehyde was produced, undetermined quantities of formaldehyde were also observed. [c] Relative to base-case (0.38 M propylene at 1.0 atm) rate: 2.93×10^{-3} M h^{-1}. [d] Millimoles of propylene oxide formed divided by millimoles of propylene converted times 100%. [e] Condensed propylene with no solvent.

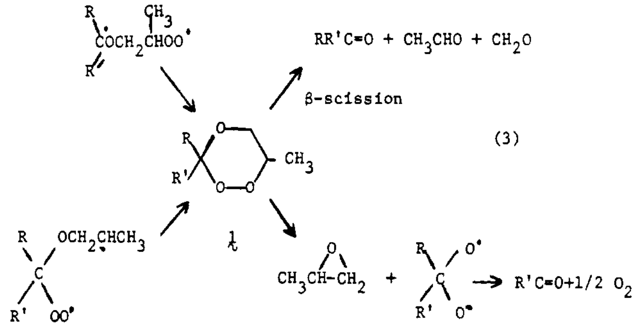
of the formation of acetaldehyde and formaldehyde.[11] At the highest propylene concentrations (9.6 and 12.2 M) acetaldehyde became the major photooxidation product. The total conversion of propylene, after reaching a maximum at 3.2 M, declined slightly but remained relatively constant at higher propylene concentrations.

The formation of acetaldehyde and formaldehyde in concentrated propylene solutions did not occur in the absence of α-diketone sensitizers, nor did it occur in the absence of light. Irradiation of α-diketone solutions containing propylene oxide also failed to produce the aldehydes. Concentrated solutions of isobutylene and 1-hexene, irradiated under pressurized epoxidation conditions (53 psia, 20 psi of O_2), produced acetone and pentanal, respectively, in addition to the expected epoxides. Therefore, it appears that the aldehydes are products of an α-diketone-sensitized photooxidative cleavage and are not due to photodecomposition of propylene oxide or sensitizers.

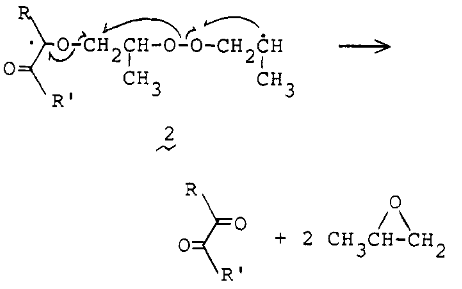
Several mechanisms for the photosensitized oxidative cleavage of propylene may be considered. Thermal or photosensitized (biacetyl) decomposition of a 1,2-dioxetane[12] formed by singlet oxygen addition to propylene is unlikely. Simple monoolefins are generally unreactive toward singlet oxygen and would be expected to undergo ene reactions to produce allylic hydroperoxides.[13] Ogata[5] has postulated a mechanism involving the fragmentation of intermediate β-benzoyloxyalkoxy radicals to explain the formation of cleavage products in the epoxidation of α-methylstyrene by acylperoxy radicals generated in the photooxidation of benzoins (eq 2). Ogata found that increasing the olefin concentration resulted in higher yields of cleavage products but did not affect the epoxide yield, suggesting that the epoxide and the cleavage products are formed from different intermediates. Our results indicate that the α-diketone-sensitized cleavage competes directly with epoxidation, suggesting that all products are formed from a common intermediate. Bartlett[6] originally proposed that the cyclic intermediate 1 could fragment to an epoxide after initial homolysis of the peroxide bond. It is conceivable that, instead of cyclizing, the resulting diradical could undergo a double β scission to produce the aldehyde products (eq 3). This pathway is similar to that observed in the thermal decomposition of ozonides;[14] however, it does not explain the increased efficiency in the production of cleavage products observed at high propylene concentrations. Bartlett has more recently suggested that epoxidation may occur by the decomposition of an oxidative polymerization intermediate, 2 (eq 4).[15] At high propylene



$$\overset{\mathrm{O}}{\overset{\|}{\mathrm{PhC}}}\mathrm{-O-CH_2-}\underset{\mathrm{Ph}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{-O^\bullet} \longrightarrow \overset{\mathrm{O}}{\overset{\|}{\mathrm{PhCCH_3}}} + \mathrm{CH_2O} + \overset{\mathrm{O}}{\overset{\|}{\mathrm{PhC}}}{}^{\bullet} \quad (2)$$



(3)



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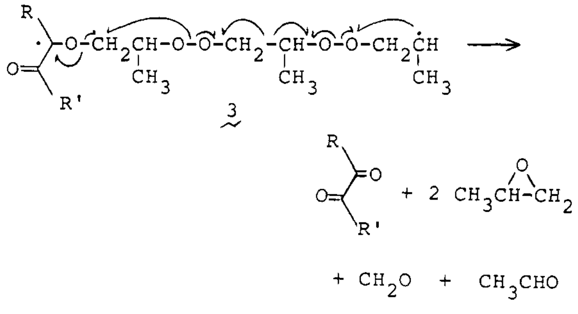

(5)

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[11] Formaldehyde was observed by gas chromatographic–mass spectral analysis of the reaction mixtures, but quantities could not be determined.

[12] (a) Kopecky, K. R.; Mumford, C. *Can. J. Chem.* **1969**, *47*, 709. (b) Turro, N. J.; Lechtken, P. *Tetrahedron Lett.* **1973**, 565.

[13] Kopecky, K. R.; Reich, H. *Can. J. Chem.* **1965**, *43*, 2265.

[14] Story, P. R.; Hall, T. K.; Morrision, W. H., III; Farine, J.-C. *Tetrahedron Lett.* **1968**, 5397.

concentrations extension of the oxidative chain would lead to intermediates (3) capable of decomposing to the cleavage products as well as epoxide (eq 5).[16]

For assessment of the efficiency of the α-diketone-sensitized photooxidation, the photon flux into the pressurized reactor was measured by potassium ferrioxalate actinometry.[17] Photon flux measurements in which light was filtered through a solution of a 2:1 mixture of 1-phenyl-1,2-propanedione and biacetyl (0.12 M, 0.5-cm path length) were subtracted from those obtained without the filter to estimate an average flux of photons capable of being absorbed by the sensitizer (~360–460 nm). Calculated quantum efficiencies of propylene conversion were near unity for pressurized reactions of $\geq$3.2 M solutions ($\Phi_{\text{propylene}} = 0.91$–$1.08$). This indicates that the propylene conversion rate under these conditions was limited by the amount of light available. By increasing the intensity of light (and the quantity of sensitizer required for its absorption), higher rates should be possible. Since the reaction products and α-diketone sensitizers appear to be stable under the reaction conditions, the high quantum efficiencies ($\Phi_{\text{propylene}}$ and Φ_{PO}; PO = propylene oxide) observed should remain high for reaction times much longer than 1.5 h, provided the appropriate propylene concentrations and oxygen partial pressures are maintained.

The observation that $\Phi_{\text{propylene}}$ did not exceed unity (within experimental error) is significant in that it suggests that the photooxidation is not a chain process. It is also important to note that under the proper conditions (3.2 M propylene, 158 psia, 18 psi of O_2) an excellent propylene oxide (PO) quantum efficiency was obtained ($\Phi_{\text{PO}} = 1.0$).

Conclusions

Pressurization (50–180 psia) effectively increased the rate of the α-diketone-sensitized photoepoxidation of propylene and other gaseous olefins, primarily by increasing the solution concentration of the olefins. Under optimal conditions propylene photoepoxidation can be highly selective and efficient. At high propylene concentrations a photooxidative cleavage reaction competes with epoxidation but a high propylene conversion efficiency is maintained. Control of the product ratio is possible by appropriate manipulation of the propylene concentration.

Although this work was not directed toward elucidating the mechanism of the photoepoxidation, several pertinent observations have been made. First, in contrast to Bartlett's observation,[6] epoxidation occurred with little or no decomposition of the α-diketone sensitizers. This may be the result of using very large olefin/α-diketone ratios (2:1 to 300:1) which would favor addition of the olefin to the excited-state diketone.[18] This lack of sensitizer decomposition is also in opposition to Ogata's contention[5] that the epoxidizing species is an acylperoxy radical formed by initial oxidative cleavage of the diketone. Furthermore, the quantum efficiency of propylene oxidation maximized at 1.0. The theoretical quantum efficiency of the Ogata mechanism, assuming two acylperoxy radicals are formed from each diketone, should be 2.0. Finally, the observation that oxidative cleavage products of propylene were formed at the expense of propylene oxide suggests the involvement of diradical intermediates of the type proposed by Bartlett.[6] A more definitive determination of the intermediates involved in the photoepoxidation and the oxidative cleavage will require further investigation.

Experimental Section

Biacetyl, benzil, *o*-dichlorobenzene and 1-hexene were purchased from Aldrich Chemical Co. 1-Phenyl-1,2-propanedione was obtained from Eastman Organics. Propylene and isobutylene were obtained from Matheson. Solutions were irradiated with a General Electric 1000-W tungsten projection lamp (Model BRH) or a Canrad-Hanovia 450-W high-pressure mercury lamp (Model 679A).

UV–visible spectra of the α-diketones were obtained with a Hewlett-Packard 8450A spectrophotometer. Photooxidation and sensitizer decomposition products were identified by gas chromatographic–mass spectral analysis with a Varian 3700 gas chromatograph interfaced with a Finnigan 4000 mass spectrometer. Quantitative analysis of reaction mixtures was done with a Varian 1700 gas chromatograph with thermal conductivity detectors by using a stainless steel, 0.125 in. × 15 ft, 5% FFAP on 80/100-mesh Chromosorb W-HP column (Alltech Associates).

General Procedure for Photoepoxidation of Propylene at Atmospheric Pressure. Reactions were run in a 250-mL cylindrical photoreactor equipped with a thermometer, a water-cooled Pyrex immersion well, and a dry ice condenser. A fritted glass disk in the bottom of the reactor allowed gases to be bubbled through the reaction mixtures. The condenser exit was connected to the gas inlet by silicone tubing (0.39 in. o.d.) so that unreacted gases could be recycled to the reactor with a tubing pump. A solution of the sensitizer in *o*-dichlorobenzene was placed in the reactor and saturated with propylene through the fritted disk. Saturation was complete when propylene began to liquify in the condenser. The propylene flow was stopped and oxygen from a gas buret was pumped through the reactor. After the system stabilized (5–10 min) the lamp was turned on. Oxygen was bubbled through the solution continuously, and the temperature was maintained at 15–18 °C by the cooling effects of the immersion well and condensing propylene. At the end of the reaction the lamp was turned off, and the solution was analyzed by GC with tetrahydrofuran as an internal standard.

An *o*-dichlorobenzene solution (250 mL) containing 2.8 g (32.6 mmol) of biacetyl was saturated with propylene (0.38 M) and irradiated with a 450-W high-pressure mercury lamp for 3 h with continuous bubbling of O_2. Products (identified by GC/MS) were carbon dioxide, propylene oxide (15.0 mmol), and acetone (1.0 mmol).

Photodecomposition of α-Diketones. A solution of *o*-dichlorobenzene (250 mL) containing 2.4 g (27.9 mmol) of biacetyl was irradiated (450-W high-pressure mercury lamp) for 3 h with continuous bubbling of O_2. GC/MS analysis showed that the irradiated mixture contained acetone (5.2 mmol) and carbon dioxide. Smaller quantities of acetone and carbon dioxide were observed upon similar treatment of a solution of *o*-dichlorobenzene (250 mL) containing 2.5 g (17.0 mmol) of 1-phenyl-1,2-propanedione. Irradiation of 2.5 g (12.0 mmol) of benzil in 250 mL of *o*-dichlorobenzene produced no detectable photoproducts.

General Procedure for the Pressurized Photoepoxidation of Propylene. Pressurized propylene photoepoxidations were run in a 750-mL glass pressure reactor with a stainless steel cover equipped with an air-driven stirrer and an internal cooling coil (Chemical Equipment Co.). The reactor was charged with *o*-dichlorobenzene containing 1-phenyl-1,2-propanedione (0.027 M) and biacetyl (0.013 M), purged with nitrogen, and then sealed. By opening an air-actuated valve, condensed propylene was charged to the reactor from a prefilled reservoir. The quantity of propylene charged was determined later by weighing the reservoir. The stirrer was started and the pressure was allowed to stabilize. Nitrogen (if required) and then oxygen were introduced to bring the reactor to operating pressure. **Warning**: Propylene and oxygen may form potentially explosive mixtures,

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[15] Bartlett, P. D., unpublished paper presented at the Frontiers of Free Radical Chemistry Symposium, Louisiana State University, April 10–11, 1979.

[16] I thank one of the referees for bringing ref 15 to my attention and for suggesting the oxidative polymerization mechanism. It should be noted, however, that this mechanism should result in propylene conversion efficiencies of >1.0 at high propylene concentrations. This is contrary to our observations.

[17] Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973; pp 119–23.

[18] Bartlett observed more rapid sensitizer decomposition with olefin/α-diketone ratios between 1:1 and 1:5.

particularly at elevated pressures. Care must be taken to avoid the use of dangerous vapor compositions (maintain ≤20% v/v O_2 at total pressures ≤200 psia[19]) and to isolate the system from potential ignition sources. The reactor should be grounded to prevent a buildup of static electricity.

The pressurized reaction mixture was irradiated for 1.5 h with a 450-W high-pressure mercury lamp in an externally positioned Pyrex immersion well. The operating pressure was maintained by periodically adding oxygen to replace that which was consumed. The temperature was maintained at 12–19 °C. Upon completion of the irradiation unreacted propylene was slowly vented (3 h), and the reaction mixture was analyzed by quantitative GC. When high concentrations of propylene were used, considerable evaporation of the volatile products occurred, requiring a modification of the sampling procedure. In these reactions a measured volume of the pressurized liquid phase was vented into an ice-cooled coil of stainless steel tubing (0.125 in. o.d.). This sample was then slowly vented into 50 mL of *o*-dichlorobenzene and analyzed by GC.

A solution of *o*-dichlorobenzene (250 mL) containing 1.4 g (9.5 mmol) of 1-phenyl-1,2-propanedione and 0.4 g (4.7 mmol) of biacetyl was placed in the pressure reactor. The reactor was purged with nitrogen and sealed before 45.6 g (1.09 mol) of propylene was charged, bringing the total volume to 339 mL[20] and the pressure to 70 psia. Nitrogen (80 psi) and oxygen (18 psi) were then charged, bringing the total pressure to 168 psia. The mixture was irradiated for 1.5 h at 12–15 °C. Sufficient oxygen was added during the reaction to maintain the pressure at 165–9 psia. The unreacted propylene was slowly vented (3 h) and the solution analyzed by GC. Propylene oxide (11.24 mmol), acetaldehyde (0.86 mmol), and formaldehyde (undetermined) were the only products observed.

Pressurized Photooxidation of 1-Hexene. A solution of 1.0 g (6.7 mmol) of 1-phenyl-1,2-propanedione and 0.28 g (3.3 mmol) of biacetyl in 250 mL of 1-hexene was placed in the pressure reactor. Nitrogen (20 psi) and oxygen (20 psi) were introduced, bringing the pressure to 54 psia. The mixture was irradiated 1.5 h at 19–20 °C and 50–54 psia. After the pressure was released, GC/MS analysis of the reaction mixture showed the formation of *n*-butyloxirane, pentanal, and formaldehyde.

Quantum Efficiency Measurements. The flux of photons from the mercury lamp into the pressurized reactor was measured by potassium ferrioxalate actinometry.[17] The average total flux was determined to be 1.84×10^{-4} einstein min^{-1} (±3%). A second series of measurements was made in which the light was filtered through a solution of 1-phenyl-1,2-propanedione (0.08 M) and biacetyl (0.04 M) in *o*-dichlorobenzene (0.5 cm path length) before entering the reactor. The average value of these measurements (5.92×10^{-5} einstein min^{-1}, ±3%) represents the flux of photons outside the absorption band of the sensitizer mixture. Subtraction of this flux from the total photon flux gave the flux of photons capable of being absorbed by the photoepoxidation system (1.25×10^{-4} einstein min^{-1}). This value was used to estimate the quantum efficiencies of propylene oxide formation and propylene conversion.

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Registry No. Propene, 115-07-1; biacetyl, 431-03-8; benzil, 134-81-6; 1-phenyl-1,2-propanedione, 579-07-7.

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[19] Zakaznov, V. F.; Kursheva, L. A.; Fedina, Z. I. *Sov. Chem. Ind. (Engl. Transl.)* 1978, *10*, 468.

[20] Based on a propylene density of 0.51 g/mL.

Synthesis of Bis(aryloxyethyl) Vinyl Ethers via Phase-Transfer-Catalyzed Nucleophilic Displacement on 2-Chloroethyl Vinyl Ether

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Bis(aryloxyethyl) vinyl ethers can be prepared in high yield by using sodium hydroxide, bis(phenols), and 2-chloroethyl vinyl ether (CEVE) with a tetraalkylammonium salt phase-transfer catalyst. The displacement reaction of the bis(phenol) dianion proceeds in high yield only if both excess CEVE and base are employed. Nucleophilic displacement is considerably faster than elimination reactions involving solvent or catalyst. Small amounts of water have little effect on the reaction. The synthesis has been extended to the preparation of related monoaryloxyethyl vinyl ethers.

Introduction

The phase-transfer-catalyzed reaction of phenolate anions and alkyl halides has been used to prepare a variety of aryl alkyl ethers.[1,2] In many of these syntheses, relatively large amounts of catalyst are employed. In addition, the bulk of literature investigations has focused on the reactions of monoanions. We report the extension of this method to the preparation of diarylalkyl vinyl ethers with efficient use of the phase-transfer catalyst. The effects of various reaction parameters, especially base concentration and moisture content, have been investigated.

In attempts to identify new materials for cationically initiated polymerization,[3] a variety of bis(aryloxyethyl) vinyl ethers were prepared. Initially, the reaction of selected bis(phenols) with excess chloroethyl vinyl ether (CEVE) and base was run in dimethyl sulfoxide (Me_2SO) solution.[4] It was thought that this reaction could be more easily accomplished by replacing Me_2SO with another solvent and employing a phase-transfer catalyst (PTC). After preliminary evaluation, the reaction of bisphenol A (BPA) with CEVE was chosen as a representative candidate for investigation (eq 1).

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[1] Dehmlow, E. V.; Dehmlow, S. S. "Phase Transfer Catalysis"; Verlag Chemie: Weinhein, West Germany, 1980.

[2] Starks, C. M.; Liotta, C. "Phase Transfer Catalysis Principles and Techniques"; Academic Press: New York, 1978; pp 126–140. Keller, W. E. "Compendium of Phase-Transfer Reactions and Related Synthetic Methods"; Fluka AG: Buchs, Switzerland, 1979; pp 70–74.

[3] Butler, G. B.; Nash, J. L. *J. Am. Chem. Soc.* 1951, *73*, 2538.

[4] Crivello, J. V.; Conlon, D. A., unpublished results.

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