83-9; 1-phenylcyclohexene, 771-98-2; 1-methyl-4-isopropyl-1,3-cyclohexadiene, 99-86-5; 1-(methyl-d_3)-4-(1-methylethyl-*1-d*)-1,3-cyclohexadiene-*5,5,6,6-d*$_4$, 87555-85-9; magnesium chloride (1-cyclohexenyl)methylsulfinate, 87555-89-3; magnesium chloride (2-methoxy-1-cyclohexen-3-yl)sulfinate, 87555-90-6; magnesium, 7439-95-4; 1,4-cyclohexadiene, 628-41-1; 1-ethyl-1,4-cyclohexidiene, 19841-74-8; γ-terpinene, 99-85-4; benzene, 71-43-2; ethylbenzene, 100-41-4; *p*-cymene, 99-87-6; ascaridole, 512-85-6; 1-chloro-2-methylenecyclohexane, 71518-98-4; 3-chloro-2-methoxy-1-cyclohexene, 59892-15-8.

Electrogenerated Bases. 8.[1] Epoxidations by Electrogenerated Superoxide with/without Auxiliary Carbon Acids. α,β-Unsaturated Ketones

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Excellent yields of the epoxides of cyclohexenone (**14**), 4,4-dimethylcyclohexenone (**15**), mesityl oxide (**17**), and benzalacetophenone (**18**) were obtained by treating the enones contained in the cathode chamber of an electrochemical cell with in situ electrogenerated superoxide in the presence of an auxiliary carbon acid such as diphenylacetonitrile (**6**) or, better, diethyl methylmalonate (**1**). Poor or no yields were obtained in the absence of the carbon acid. Products previously prepared by the reaction of electrogenerated superoxide with these carbon acids alone were formed here as coproducts. A rationalization is offered for the effectiveness of this methodology and an explanation of the difference between these results and those that had been reported by others using potassium superoxide/18-crown-6 as an epoxidant.

The development of new methods and new features of epoxidation continues to be a very active area of research.[3] Of the variety of epoxidizing systems that have been employed, those using dioxygen or its derivatives are most relevant to the work reported here: (a) O_2 + Ag ± dopant ± a support;[4a] (b) O_2 and a transition metal ion, often with AIBN;[4b] (c) singlet oxygen produced photochemically in the presence of a sensitizer;[4c] (d) derivatives of H_2O_2 such as HO_2^-, peracids, *t*-BuOO$^-$, and peroxyamidic acids;[5] (e) superoxide[6] with/without an "adjunct reagent"; (f) α-hydroperoxy carbonyl compounds.[7]

We report here a new methodology for epoxidizing olefins. The scope and limitations of this method are to be determined. We have chosen to use first α,β-unsaturated ketones as substrates because the results are novel, are synthetically useful, and may also serve to clarify some of the discrepancies in the literature concerning attempted epoxidations of this subgroup of olefins (vide infra).

Superoxides with R_4N^+ counterions are most conveniently prepared by electrochemical one-electron reduction of oxygen (O_2) in aprotic media containing R_4NX electrolytes. They are readily soluble in organic solvents. *Since only part of the oxygen (O_2) supplied to the cathode compartment of a cell is reduced, the intermediates, if formed by reaction of superoxide with substrates, have the opportunity directly upon their generation to react with excess dissolved oxygen.* This is different from the situation that obtains when KO_2/18-crown-6 is the reagent: the latter makes oxygen available only in semimolar quantity when it is functioning as an electron-transfer agent.[8] The special features of the electrochemical method have led to the development of a number of useful syntheses which involve oxygenation of appropriate[9] carbon acids *under reducing conditions*.[1,10]

The selected examples shown in eq 1–3 illustrate oxygenation of the starting material at the α-position and three types of concomitant consequences for the electron-withdrawing groups (EWGs): (1) the EWGs remain intact (eq 1); (2) they are partially cleaved (displaced) (eq 2); (3) they are totally displaced (eq 3). It has been suggested[10a] that these transformations occur by the following steps: (1) superoxide, as an electrogenerated base (EGB) deprotonates the carbon acid; (2) the resulting carbanion reacts with oxygen (in several electron-transfer steps)[11] to yield the hydroperoxy anion; (3) the latter evolves into the

$$\underset{\mathbf{1}}{\mathrm{MeCH(COOEt)_2}} \xrightarrow[\substack{O_2\\ \mathrm{DMF}\\ \mathrm{Et_4NBr}\\ \mathrm{Hg}\\ -1.0\ \mathrm{V\ vs.\ SCE}}]{} \underset{\mathbf{2}\ (95\%)}{\mathrm{MeC(OH)(COOEt)_2}} \tag{1}$$

$$\underset{\mathbf{3}}{\mathrm{PhCH(COOEt)_2}} \xrightarrow[\substack{\text{same}\\ \text{conditions}}]{} \underset{\mathbf{4}\ (74\%)}{\mathrm{PhCOCOOEt}} + \underset{\mathbf{5}\ (7\%)}{\mathrm{PhC(OH)(COOEt)_2}} \tag{2}$$

$$\underset{\mathbf{6}}{\mathrm{Ph_2CHCN}} \xrightarrow[\substack{\text{same}\\ \text{conditions}}]{} \underset{\mathbf{7}\ (95\%)}{\mathrm{Ph_2CO}} + \mathrm{CN^-} \tag{3}$$

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[1] Paper 7: Sugawara, M.; Baizer, M. M. *Tetrahedron Lett.* **1983**, *24*, 2223.

[2] Department of Applied Chemistry, Yamagata University, Yonezawa, Yamagata-ku 992, Japan.

[3] (a) A review of the *synthetic* work published between July 1980 and June 1981 has 93 references: Mason T. J. In "Heterocyclic Chemistry"; The Royal Society of Chemistry: London, 1982; Vol. 3, pp 1–47. (b) An excellent discussion of earlier work is given by: House, H. O. "Modern Synthetic Reactions", 2nd ed.; Benjamin/Cummings Publishing Co.: Menlo Park, CA, 1972; pp 296–319. (c) After this work was completed, we gained access to Frimer's superb review: Frimer, A. A. "The Organic Chemistry of Superoxide Anion Radical in Superoxide Dismutase"; Oberley, L. W., Ed.; CRC Press: Boca Raton, FL, 1982; Vol. II, pp 83–125.

[4] (a) Reference 3a, p 2. (b) Kaneda, K., Jitsukawa, K.; Itoh, T.; Teranishi, S. *J. Org. Chem.* **1980**, *45*, 3004. (c) Paquette, L. A., Bellamy, F.; Boehm, M. C. *Ibid.* **1980**, *45*, 4913.

[5] Sawaki, Y.; Ozatu, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 793 and references therein.

[6] (a) In all but one case, discussed later, it was supplied by KO_2 or, for better solubility in organic media, KO_2/18-crown-6. (b) Valentine, J. S.; Curtis, A. B. *J. Am. Chem. Soc.* **1975**, *97*, 224.

[7] Rebek, J., Jr.; McCready, R.; Wolak, R., *J. Chem. Soc., Chem. Commun.* **1980**, 705.

[8] It is well-known that superoxide is a multipotent reagent.[3c] Depending upon the demands of the substrate, it may serve as a nucleophile, as a base, as an electron-transfer reagent, or as a radical. Of course, additional oxygen could be supplied from an external source.

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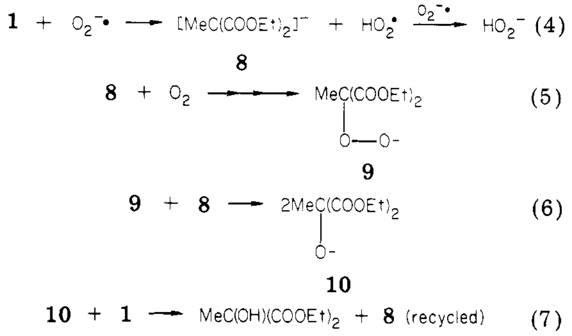
Scheme I

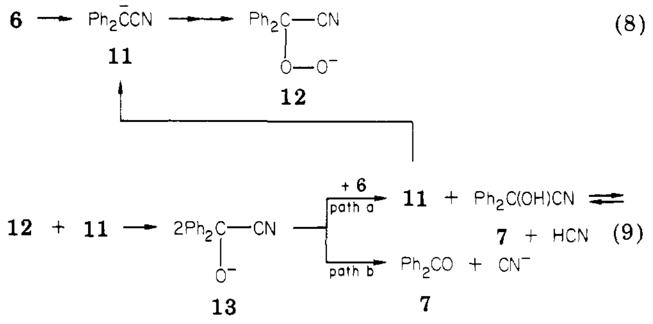

$$\mathbf{1} + O_2^{-\bullet} \longrightarrow [MeC(COOEt)_2]^- + HO_2^\bullet \xrightarrow{O_2^{-\bullet}} HO_2^- \quad (4)$$

$$\mathbf{8} + O_2 \longrightarrow \underset{\mathbf{9}}{MeC(COOEt)_2(O{-}O^-)} \quad (5)$$

$$\mathbf{9} + \mathbf{8} \longrightarrow \underset{\mathbf{10}}{2MeC(COOEt)_2(O^-)} \quad (6)$$

$$\mathbf{10} + \mathbf{1} \longrightarrow MeC(OH)(COOEt)_2 + \mathbf{8}\ \text{(recycled)} \quad (7)$$

Scheme II


$$\mathbf{6} \longrightarrow \underset{\mathbf{11}}{Ph_2\bar{C}CN} \longrightarrow \underset{\mathbf{12}}{Ph_2C(O{-}O^-){-}CN} \quad (8)$$

$$\mathbf{12} + \mathbf{11} \longrightarrow \underset{\mathbf{13}}{2Ph_2C(O^-){-}CN} \begin{cases} \xrightarrow[\text{path a}]{+\mathbf{6}} \mathbf{11} + Ph_2C(OH)CN \rightleftharpoons \mathbf{7} + HCN \\ \xrightarrow{\text{path b}} \underset{\mathbf{7}}{Ph_2CO} + CN^- \end{cases} \quad (9)$$

final products. Since, in many cases, no more than 1 F/mol is required to consume the entire substrate, some catalytic sequence must also be involved when the EWG is not displaced.

Equations 1–3 may now be expanded to eq 4–7 (Scheme I). When **6** is the carbon acid involved, the intermediate **13** may deprotonate **6** at least to some extent and continue the catalytic cycle (path a, Scheme II) or it may expel the EWG (path b) and interrupt the cycle. Indeed, the preparation of **2** in 95% yield required only 0.17 F/mol of **1** while the formation of **7** in the same yield required 0.8 F/mol of **6**. [In both cases a second epoxidizing agent, $R_4N(HO_2)$, is also produced.]

It will be noted that the hydroperoxy intermediates such as **9** and **12** are precisely of the type that has been used recently in epoxidations.[12] Inclusion of olefins of appropriate structure[9] at the beginning of an electrolysis should allow them to intercept at least a portion of **9** and/or **12** and lead to oxiranes. This proved indeed to be the case. We conclude that for successful epoxidation to occur *it is necessary that a carbon acid, either the olefinic substrate itself or a purposely added "adjunct reagent" capable of forming hydroperoxides from* $O_2^- + O_2$ *be present in the reaction mixture.*

Three consequences of using this electrochemical methodology for epoxidations are to be expected: (1) the yields of epoxides will depend upon the rates of reaction of the hydroperoxides with the olefins relative to the rate of formation of "normal" products from say **9** and **12** in the absence of olefin; (2) insofar as diversion of **9** and **12** from their roles in Schemes I and II will interrupt the catalytic cycles leading respectively to **2** and **7**, more than 1 F/mol of substrate will be required especially in the case of **13** (from **12**) which already has two routes of decomposition; (3) due to the competitive pathways mentioned in consequence 1 for the follow-up reactions of **9** and **12**, more than 1 mol of carbon acid/mol of enone may be required for satisfactory epoxidation. The conclusions of this analysis[13] were borne out by our experimental results.

The behavior of the cyclohex-2-en-1-ones **14**–**16** illustrates several of the considerations discussed above. It is well-known that **14** belongs to the class of compounds[14] which are both Michael acceptors and Michael donors; **14** can therefore readily be dimerized, trimerized, etc. by a variety of basic catalysts including EGBs.[15] Frimer and Gilinsky reported[16] that superoxide (from KO_2/18-crown-6), functioning as a base, also catalyzed these Michael reactions; they could not duplicate the formation of the **14** epoxide which had been obtained in 30% yield by Dietz et al.[17] using *electrogenerated superoxide.* It seems clear now that in the absence of excess oxygen the anion of **14** has too little opportunity to form a hydroperoxide, essential for the epoxidation reaction, and reacts by the available alternative pathway (Michael reaction). However, we have confirmed the results reported by Dietz et al.[17] (Table I, expt 1). Further, if the synthetic objective is to prepare **14** epoxide, it is more advantageous to use an auxiliary carbon acid of lower pK_a than **14** as a precursor of *some* required hydroperoxide rather than to consume some of **14** for that purpose. Experiments 2 and 3 demonstrate the enhancement of yield of **14** epoxide by using this strategy. Of course now **12** not only epoxidizes **14** but also independently forms **7** (eq 9). While a respectable yield of **14** epoxide (expt 2) is produced on using **6**/**14** in a molar ratio 1:1, an excellent yield (expt 3) is obtained when the ratio is 2:1. *It is an inevitable consequence of this methodogy that a cathodic coproduct, often very useful per se, must be formed.* The possibility still exists of combining these cathodic processes with a simultaneous useful anodic process in a "paired" reaction.

When the "active" hydrogens of **14** are partially (**15**) or totally (**16**) replaced by methyl groups, epoxidation of the substrate becomes increasingly difficult. With KO_2 **15** yielded no epoxide,[16,18] and **16** was "totally inert even after several days of mixing". By our procedure **15** gave 9.5% of epoxide (expt 4) when treated with electrogenerated superoxide and only a trace when **6** as included as an "adjunct reagent" (expt 5); **16** yielded no epoxide (expts 9 and 10). We conclude that when the intermediate hydroperoxides must arise from substrate alone, steric factors block most (**15**) or all (**16**) of the epoxidation. The situation was not improved by including in situ **12** because the latter can too readily decompose to **7** (eq 8 and 9). However, inclusion of in situ prepared **9**, which does not decompose by intramolecular displacement of an EWG and is available to react even with an unfavorable substrate, did lead to **15** epoxide (expts 6–8).

The acyclic enones **17** and **18** were also epoxidized by electrogenerated superoxide (plus oxygen) and **6**. Molar ratios of 4:1 of **6**/enone were necessary to achieve good yields of the respective epoxides. In the absence of **6** (expt 15) benzoic acid (83%) was the major product from **18**. It had been reported previously[19] that KO_2/18-crown-6 acted

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[9] E.g., when RH is of adequately low pK_a and of a composition which does not permit it to be reduced more readily than is O_2.

[10] (a) Allen, P. M.; Hess, U.; Foote, C. S.; Baizer, M. M. *Synth. Commun.* **1982**, *12*, 123. (b) Sugawara, M.; Baizer, M. M.; Monte, W. T.; Little, R. D. *Acta Chem. Scand. Sect. B*, in press.

[11] Russell, G. A.; Janzen, E. J.; Bemis, A. G.; Geels, E. J.; Moyes, A. J.; Mak, S.; Strom, E. T. *Adv. Chem. Ser.* **1965**, *No. 51*, 112, 139.

[12] In ref 7 the authors recommended the reagents $Ph_2C(OOH)COOMe$ and $Ph_2C(OOH)CN$.

[13] Retrospective, as is so frequently the case.

[14] An acyclic example is diethyl glutaconate.[15]

[15] Baizer, M. M.; Chruma, J. L.; White, D. A. *Tetrahedron Lett.* **1973**, 5209.

[16] Frimer, A. A.; Gilinsky, P. *Tetrahedron Lett.* **1979**, 4331.

[17] Dietz, R.; Forno, A. E. J.; Larcombe, B. E.; Peover, M. E. *J. Chem. Soc.* **1970**, *816*.

[18] The primary product was 2-hydroxy-4,4-dimethylcyclohexa-2,5-dien-1-one.

Table I. Epoxidations of Enones with Electrogenerated Superoxide with and without Carbon Acids[a]

expt 1	enone (5 mmol)	carbon acid	mmol	est pK_a[b]	Faradays/mol of enone	yield of epoxide, %	recovd enone, %	coproduct
1	2-cyclohexen-1-one (**14**)	Ph_2CHCN (**6**)	0		2.0	40	35	
2			5.0	17.5	0.9	67	18	Ph_2CO (**7**)
3			10.0		1.8	89	trace	**7**
4	4,4-dimethyl-2-cyclohexen-1-one (**15**)	**6**	0		1.2	9.5	81	
5			10.0	17.5	1.8	trace	85	**7**
6			10.0		0.45	31	59	$CH_3C(OH)(COOEt)_2$[c] (**2**)
7		$CH_3CH(COOEt)_2$ (**1**)	20.0	15–16	0.88	56	38	**2**
8			40.0		1.80	90	trace	**2**
9	4,4,6,6-tetramethyl-2-cyclohexen-1-one	**6**	0		1.0		87	
10			10.0	17.5	1.8		85	**7**
11	$Me_2C{=}CHCOMe$ (**17**)	**6**	0		1.0	3	83	
12			5.0	17.5	0.9	15	64	**7**
13			10.0		1.9	42	35	**7**
14			20.0		3.7	85	trace	**7**
15	$PhCH{=}CHCOPh$ (**18**)	**6**	0		3.0	trace		**7**
16			5.0	17.5	0.7	23	65	**7**
17			10.0		1.6	42	39	**7**
18			20.0		3.2	84	trace	**7**

[a] For conditions see the Experimental Section. [b] Equilibrium acidities in Me_2SO have been reported in a number of publications by F. G. Bordwell and co-workers. The pK_a of **6** is given at 17.5 by: Bordwell, F. G.; Bares, J. E.; Bartmess, J. E.; McCollum, G. J.; Van der Puy, M.; Vanier, N. R.; Matthews, W. S. *J. Org. Chem.* **1977**, *42*, 321. *In the same system* dimethyl malonate has a pK_a of 15.7 from which we have made an estimate of 15–16 for **1**: Bordwell, F. G. *Pure Appl. Chem.* **1977**, *49*, 963. The pK_a of **14** has not been reported; we base our estimate of 21–22 on the fact that cyclohexanone has a pK_a of 26.4 (Borawell, loc. cit.). The same *relative* orders of acidity should obtain in our solvent system. [c] 94% yield; not determined in experiments 7 and 8.

as an electron-transfer reagent[8] toward **18** and cleaved it to benzoic and phenylacetic acids in benzene solution saturated with oxygen.

The scope of this methodolgy for epoxidation is being further studied in collaboration with Professor Tetsuo Osa of Tokoku University, Sendai, Japan. Other olefins and auxiliary carbon acids are being examined.

Experimental Section

Recent papers in this series[1,10b,20] have discussed the electrochemical H-cell, the potentiostat and coulometer, and the analytical equipment and techniques used. The cathode was mercury (ca. 7.1 cm^2) and the anode a platinum foil (ca. 6.25 cm^2). The supporting electrolyte, as in the papers cited, was tetra-*n*-butylammonium bromide. The solvents used, DMF (expts 1, 4, 9, 11, 15, 17) and acetonitrile (in all other cases) were especially purified and dried. The DMF (Mallinckrodt) was stirred with calcium hydride under nitrogen for 2 days, decanted, stirred with anhydrous copper sulfate under nitrogen for 2 days, distilled at 40 °C (10 torr), stored over 3A molecular sieves, and finally passed through a column of activated alumina (Aldrich) just prior to use. The acetonitrile was distilled from phosphorus pentoxide, stored over 3A molecular sieves, and given the final drying by alumina as above. Silica gel (Merck silica 60, 230–280 mesh) was used for column chromatography.

Cyclohexenone (**14**) and mesityl oxide (**17**) were purchased from Mallinckrodt and redistilled. Chalcone (**18**)[21] and 4,4-dimethyl-2-cyclohexenone (**15**)[22] were prepared by methods described in the literature. 4,4-6-Trimethyl-2-cyclohexenone[23] was methylated[24] to **16**.

Reference samples of the epoxides were prepared by known methods from cyclohexenone (**14**),[25] mesityl oxide (**17**),[25] chalcone,[25] 4,4-dimethyl-2-cyclohexenone (**15**),[26] and 4,4,6,6-tetramethyl-2-cyclohexenone.[26,27] The identity of the electrochemically prepared epoxides with the respective reference samples was established by TLC, GC, and IR spectroscopy. The reference sample of diethyl methyltartronate (**2**) was prepared as previously.[10a]

Two representative epoxidation procedures are described below, one in which the enone alone was involved (DMF solvent) and one in which the enone and an auxillary carbon acid were used (CH_3CN solvent). Any deviations from the "normal" are indicated.

Epoxidation of 2-Cyclohexen-1-one (14) Alone (Expt 1). To the cathode compartment (ca. 60 mL) of the thoroughly dried H-cell were added 60 mL of 0.2 M tetra-*n*-butylammonium bromide in DMF, 5.0 mmol of **14**, and ca. 10 g of activated alumina. The anode compartment was charged with the same volume of the solvent/electrolyte system containing also 1 mL of cyclohexene (to trap anodically generated bromine). Purified dry oxygen[8b,18] was bubbled through the catholyte for 30 min, and then electrolysis at 60–70 mA was begun at a potentiostatically controlled cathode voltage of −1.0 V vs. SCE and continued until 2 F/mol of **14** had been passed.[28] Most of the DMF was removed from the catholyte by vacuum fractionation (Vigreux column) at 40 °C (5 torr). The residue was extracted with ether (electrolyte insoluble), washed with water, dried over anhydrous magnesium sulfate, and then concentrated. The residue was separated into its components by column chromatography using Skellysolve–ether (5:1) as eluent: fraction 1, **14**; fraction 2, **14** epoxide. The

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(19) Rosenthal, I.; Frimer, A. *Tetrahedron Lett.* **1976**, 2805.

(20) Monte, W. T.; Baizer, M. M.; Little, R. D. *J. Org. Chem.* **1983**, *48*, 803.

(21) Kohler, E. P.; Chadwell, H. M. "Organic Syntheses"; Wiley: New York, 1942; Collect. Vol. I, 71.

(22) Chen, Y.; Epstein, W. W. *Org. Synth.* **1973**, *53*, 48.

(23) Cook, K. L.; Waring, A. J. *J. Chem. Soc., Perkin Trans 1* **1973**, 529.

(24) Russell, G. A.; Stevenson, G. R. *J. Am. Chem. Soc.* **1977**, *93*, 2432.

(25) Yang, N. C.; Finnegan, R. A. *J. Am. Chem. Soc.* **1958**, *80*, 5845.

(26) Langin-Lanteri, M. T.; Huet, J. *Synthesis* **1976**, 541.

(27) Felix, D.; Wentner, C.; Eschenmoser, A. *Org. Synth.* **1976**, *55*, 52.

(28) In this case, because of poor conversion, the termination point was arbitrary. In all other cases the progress of the electrolysis was monitored by TLC, and the reaction terminated when the enone or the auxiliary carbon acid had been totally consumed.

identity of this epoxide with an authentic sample was established by TLC, IR, and GC (6% SE-30, 0.5-m column).

Epoxidation of 4,4-Dimethylcyclohex-2-en-1-one (15) in the Presence of Diethyl Methylmalonate (2) (Expts 6–8). The cathode compartment was charged with 60 mL of 0.2 M tetra-*n*-butylammonium bromide in acetonitrile, 5.0 mmol of **15**, and the quantity of **2** indicated in Table I. The anolyte contained this solvent/electrolyte system and 1.0 mL of cyclohexene. The above electrolysis was carried out, monitored by GC and TLC for consumption of **2**, and terminated when **2** had been totally consumed. The solvent was removed from the catholyte under reduced pressure (rotary evaporator). The residue was triturated several times with ether and filtered to remove the supporting electrolyte. The residue remaining after removal of the ether was fractionated by column chromatography (ether/Skellysolve, 1:5) into (1) the tartronate **2**, (2) starting enone, and (3) the epoxide. The yields of substances in fractions 2 and 3 were determined by GC (6% SE-30, 4 mm × 5 m column) using acetophenone as an internal standard.

Epoxidation of Cyclohexenone (14) in the Presence of Diphenylacetonitrile (6) (Expts 2 and 3). The electrolysis and initial segregation of the products were carried out as above. The ether residue was partially purified by bulb-to-bulb distillation (80 °C bath temperature, 5 torr). The distillate was subjected to column chromatography (eluent Skellysolve/ether, 5:1): (a) trace of **7**, (b) recovered **14**, (c) cyclohexenone epoxide.

This workup procedure was followed in expts 4, 5, 10, and 12–14.

Attempted Epoxidation of Chalcone (17) Alone. After passage of 3.0 F/mol of the enone, **17** had all been consumed. The catholyte (DMF was the solvent in this case) was poured onto ice–water and acidified with hydrochloric acid to pH 3. The solution was extracted with three 100-mL portions of ether. The extracts were washed, dried over $MgSO_4$, and taken to dryness. The residue was only benzoic acid.

Epoxidation of Chalcone (17) in the Presence of Diphenylacetonitrile (6). In view of the cleavage reaction described above, electrolyses in expts 16–18 were continued until only ca. 90% of **6** had been consumed. The workup was "normal" as defined above.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We express thanks to our colleague, Professor B. Rickborn, for a discussion of the estimated pK_a values given in Table I.

Registry No. **1**, 609-08-5; **6**, 86-29-3; **14**, 930-68-7; **14** epoxide, 6705-49-3; **15**, 1073-13-8; **15** epoxide, 1074-26-6; **16**, 32264-57-6; **16** epoxide, 87482-82-4; **17**, 141-79-7; **17** epoxide, 4478-63-1; **18**, 94-41-7; **18** epoxide, 5411-12-1; superoxide, 11062-77-4.

Mechanism of Photoepoxidation of Olefins with α-Diketones and Oxygen

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The benzil- and biacetyl-sensitized photoepoxidation of olefins in the presence of oxygen has been studied. The photolytic loss of diketone is not affected by the presence of olefins; the ratio of epoxide formation to diketone consumption is in the range of 1–3. An ^{18}O-tracer study shows that the epoxide oxygen derives from molecular oxygen and that the recovered oxygen does not scramble. The photoepoxidation is accompanied by C–C bond cleavage; the ratio of epoxidation to C–C scission is not affected by solvent polarity and only slightly affected by the presence of diazabicyclooctane (Dabco). These results are explained by a mechanism involving the addition of oxygen to triplet diketone to give an acylperoxy radical, which is a key epoxidizing species.

Many photooxidations of olefins go by a singlet oxygen mechanism (the so-called type II photosensitized oxidation[1]). The products of this reaction are principally hydroperoxides. A second well-known process, called the type I reaction, proceeds by hydrogen atom or electron abstraction by the excited sensitizer. It has recently been reported that olefins can be photoepoxidized by diketone sensitizers and oxygen, and that the reaction is quite different from either the type I or type II photooxidation.[2a,b] More recently, α-diketone-sensitized photoepoxidation has been used as a preparative epoxidation method.[3a,b,d] Epoxide formation also accompanies the reaction of singlet oxygen with some olefins,[4a–d] although (at least in some cases) it may not be a singlet oxygen product.[4e,f] Epoxides are also a significant byproduct in some electron transfer sensitized oxygenations.[5]

We now report a detailed study of the α-diketone sensitized photooxidation of olefins, focusing on the primary photoprocess and the epoxidizing species. After the completion of our study, a paper by Schuster et al.[3c] appeared on photoepoxidation with acenaphthenequinone as sensitizer. Bartlett et al. also reported an ^{18}O-tracer study of the photooxidation.[2c]

Results and Discussion

Stoichiometry. In benzene, benzil reacts photochemically in the presence of oxygen to give benzoic acid, phenyl benzoate, biphenyl, and benzoyl peroxide or phenol.[6] In

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