any series of compounds with different activation energies (and different $\Delta H^{\ddagger}$) will give rise to a LFER which is temperature dependent. Figure 4 illustrates this nicely; in the 2-alkoxytetrahydropyran series, 2-(2,2,2-trifluoroethoxy)tetrahydropyran has the lowest $\Delta H^{\ddagger}$ (by 5 kcal mol^{-1}) and thus as the temperature is increased, the entire nature of the $\sigma^*\rho^*$ plot changes. Indeed, it appears that if the temperature could be raised sufficiently high, the hydrolysis mechanism would be Scheme II (A1) for all the acetals. This observation is independent of what function one uses to scale the substituent effect; thus if pK_{ROH} is used rather than σ^* in Figure 4, the β values generated are −0.065 and +0.083 at 25 and 75 °C, respectively.

The important conclusion to be reached for the 2-alkoxytetrahydropyrans is that the substituent effect is fortuitously near zero at 25 °C because of the change in mechanism. It appears that the $A_{SE}2$ mechanism has a very slightly positive ρ^* (negative β), while the A1 mechanism has a slightly negative ρ^* (positive β). These observations are further support for the mechanisms given in Scheme III.

The Reaction Mechanism. Our data, in its entirety, are most supportive of an A1 hydrolysis mechanism for 2-ethoxytetrahydropyran, an $A_{SE}2$ hydrolysis mechanism for 2-(2,2,2-trifluoroethoxy)tetrahydropyran (and benzaldehyde *O*-ethyl *O*-2,2,2-trifluoroethyl acetal), and a modified $A_{SE}2$ mechanism for the hydrolysis of benzaldehyde diethyl acetal. Since unstrained hemicyclic acetals hydrolyze by an A1 mechanism when the leaving group is poor (e.g., ethanol), it is not surprising that a recent report[19] could find no difference in the mechanisms of hydrolysis of an unstrained bicyclic acetal and one which was constrained so as to disfavor an $A_{SE}2$ mechanism. On the basis of our results, it would be necessary to fluorinate the leaving group in order to make the mechanism become $A_{SE}2$ for these types of acetals.

Acknowledgment. Support from the National Science Foundation (CHE7907588 and PRM7919451) is gratefully acknowledged. The kind hospitality of the Chemistry Department at the University of California, Irvine, was much appreciated during a 1981–82 sabbatical leave (J. L.J.) from CSULB.

Registry No. 2-Ethoxytetrahydropyran, 4819-83-4; 2-methoxytetrahydropyran, 6581-66-4; 2-(2-methoxyethoxy)tetrahydropyran, 4819-82-3; 2-(2-chloroethoxy)tetrahydropyran, 5631-96-9; 2-(2-propynyloxy)tetrahydropyran, 6089-04-9; 2-(2,2,2-trifluoroethoxy)tetrahydropyran, 16408-83-6; acetic acid, 64-19-7; potassium acetate, 127-08-2.

Supplementary Material Available: Figures S1 and S2, kinetic plots of experimental data (2 pages). Ordering information is given on any current masthead page.

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[19] Wann, S. R.; Kreevoy, M. M. *J. Org. Chem.* **1981**, *46*, 419.

[20] Jensen, J. L.; Carr, M. D.; Yamaguchi, K. S. *Int. J. Chem. Kinet.* **1983**, *15*, 235–248.

[21] The pH of a 10^{-2} N HCl solution, μ = 0.5 (KCl), is 2.07 not 2.00; similarly, the pH of a 10^{-1} N HCl solution, μ = 0.1, is 1.10 not 1.00.[22]

[22] (a) Weast, R. C., Ed. "Handbook of Chemistry and Physics," The Chemical Rubber Co., Cleveland, Ohio, 1969, p. D102-3. (b) Long, C. Ed. "Biochemists Handbook," D. van Nostrand Co., Inc., New York, N. Y., 1968, p 30. (c) J.L.J., unpublished work (cf ref 3 and 20).

Reactions of Diphenylcyclopropenone and Tetracyclones with Potassium Superoxide

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Reactions of diphenylcyclopropenone and various tetracyclones with potassium superoxide are reported.

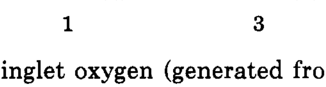
Introduction

The use of potassium superoxide as a versatile synthetic reagent has increased rapidly since the discovery[1] that it is solubilized in nonpolar solvents by crown ethers. Studies of superoxide radical anion prepared this way have led to the conclusion that $O_2^-\cdot$ reacts more as a nucleophile than as an oxidizing agent.[2] With carbonyl compounds, the predominant pathway is that of addition/elimination.[3]

The reactions of the annelones diphenylcyclopropenone (**1**) and tetracyclone (**2**) with potassium superoxide solubilized with crown ether were of interest to us in the context of a search for competitive chemical traps for superoxide/singlet oxygen.[4] Though there are reliable tests both for singlet oxygen and for superoxide radical anion, tests for $O_2^-\cdot$ in the presence of singlet oxygen and vice versa with organic trapping reagents are less well defined. At the outset, we point out that both annelones fail as competitive test systems for O_2^1 $O_2^-\cdot$ for reasons that shall become apparent.

We report herein reactions of diphenylcyclopropenone and various tetracyclones (tetraphenylcyclopentadienones) with potassium superoxide.

Reactions of Diphenylcyclopropenone with KO_2. Diphenylcyclopropenone (**1**) reacts with nucleophiles as a consequence of the large contribution of mesomeric structures **3**. A recent paper[5] suggested the ($_{\pi}2_s$ + $_{\pi}2_s$) addition of singlet oxygen (generated from the thermal decomposition of K_3CrO_8) to **1** and prompted us to in-



1 3

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[1] Valentine, J. S.; Curtis, A. B. *J. Am. Chem. Soc.* **1975**, *97*, 224.

[2] San Filippo, J.; Chern, C.; Valentine, J. S. *J. Org. Chem.* **1975**, *40*, 1678.

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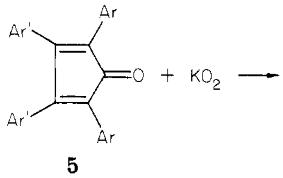
[5] Gurumurthy, R.; Narasimhan, K. *Ind. J. Chem.* **1979**, *18B*, 4.

Table I. Structures of Symmetrically Substituted Tetracyclones 5a–e



5

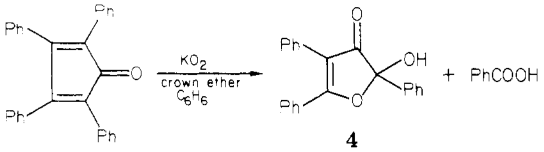
5	substituent	
	C_2, C_5	C_3, C_4
a	phenyl	*p*-tolyl
b	phenyl	*p*-chlorophenyl
c	phenyl	*p*-anisyl
d	*p*-chlorophenyl	*p*-anisyl
e	*p*-anisyl	*p*-chlorophenyl

vestigate the reaction of 1 with $O_2^-\cdot$ since we expected that reaction to be faster than that of singlet oxygen.

Diphenylcyclopropenone (1) and 2 equiv of powdered KO_2 were added to a solution containing dicyclohexano-18-crown-6 in benzene. The mixture was then stirred in the dark and protected from moisture.

The reactions were quenched after approximately a week by the addition of water and extracted with ether. The aqueous layer was worked up after acidification (1 N HCl). TLC of the crude product exhibited only two materials in the organic layer. The two compounds were benzil and unreacted 1. The extract from the acidified layer afforded benzoic acid as the only product.

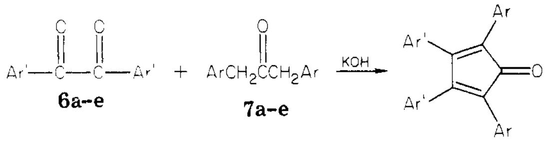
Reactions of Tetracyclone with KO_2. Rosenthal[6,7] originally studied the reaction of tetracyclone (2,3,4,5-tetraphenylcyclopentadienone) 2 with KO_2. Substituted furanone 4 was the identified product along with benzoic acid.



2 4

Rosenthal suggested the first step to be electron transfer from $O_2^-\cdot$ to the enone. This was followed by reaction of the radical anion with molecular oxygen.

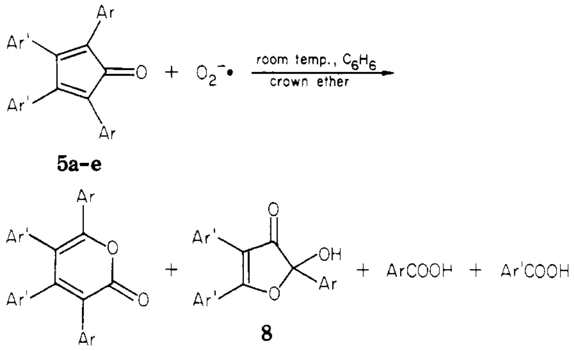
We have studied the reactions of symmetrically substituted tetracyclones 5a–e (Table I) with KO_2 and found the reaction to be more complex than originally suggested.[6,7]



6a–e 7a–e 5a–3

Tetracyclones 5a–e were synthesized by the condensation of the appropriate benzil 6 with the proper dibenzylacetone 7. Dichlorobenzil was prepared by Mohrig's method[8] by using thiamine hydrochloride as the catalyst for the benzoin condensation (see Experimental Section).

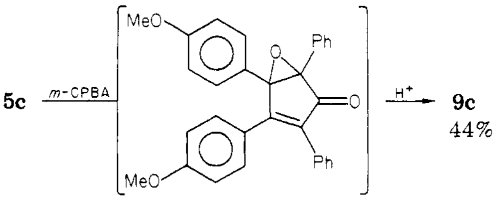
In a typical experiment, finely powdered KO_2 was added to a vigorously stirred mixture of a tetracyclone and dicyclohexano-18-crown-6 in dry benzene at room temperature, and the resulting mixture was protected from light and moisture and allowed to stir until the color changed to yellow (usually overnight). The mixture was then cautiously treated with water and the organic layer extracted with ether. After removal of the solvent the residue was chromatographed on silica with CH_2Cl_2 and then CH_2Cl_2/acetone 9:1 was added to elute the polar fractions. The aqueous layer was acidified (1 N HCl) and also extracted with ether to afford the acid. A mixture of both possible acids ($ArCO_2H$ and $Ar'CO_2H$) (Table I) was formed in all cases. A series of pyranones were obtained in the organic layer along with Frimer''s previously reported furanones.



5a–e

9a–e 8

The substitution pattern of the isolated 2-pyrones was confirmed spectroscopically as well as by independent synthesis. Epoxidation of 5c with *m*-chloroperbenzoic acid (*m*-CPBA), a route which provides a better yield than the traditional procedure[9] using H_2O_2/pyridine, gave 9c (44%).



5c 9c 44%

The question arises if the formation of 2-pyrones from KO_2 and tetracyclones 5a–e does not just proceed via epoxidation by KO_2. This suggestion is supported by formation of the epoxide from cyclohexenone and electrogenerated superoxide.[10] However, the reaction of 4,4- and 6,6-disubstituted cyclohexenones with KO_2 crown ether[11] revealed that when there is a formation of epoxide the initiation step in its formation is the base catalyzed abstraction of a proton. In the absence of hydrogens α to the carbonyl group, there was no reaction between the cyclohexadienone and superoxide. Because there are no abstractable hydrogens present in the tetracyclones (5) an epoxidation process cannot be expected.

Discussion

Benzil is formed from diphenylcyclopropenone in a reaction initiated by electron transfer from superoxide. The initial step affords the radical anion,[12] which is known to form benzil in the presence of oxygen.[12] Benzoic acid is then formed by reaction of benzil with KO_2. A mechanism

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[6] Poupko, R.; Rosenthal, T. *J. Phys. Chem.* **1973**, *77*, 1722.

[7] Rosenthal, T.; Frimer, A. *Tetrahedron Lett.* **1975**, 3731; **1976**, 2805.

[8] Mohrig, J. R.; Neckers, D. C. In "Laboratory Experiments in Organic Chemistry"; D. VanNostrand: New York, 1979; p 268.

[9] Dunston, J. M.; Yates, P. *Tetrahedron Lett.* **1964**, 505.

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

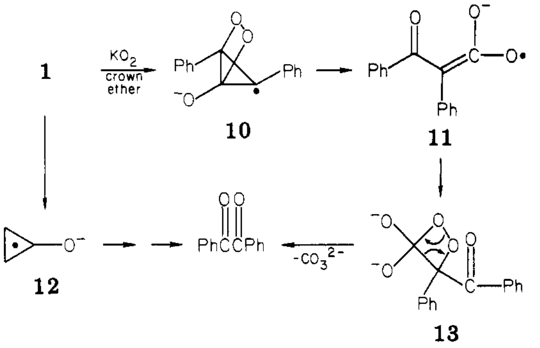
[12] Furderer, P.; Gerson, F.; Krebs, A. *Helv. Chim. Acta* **1977**, *60*, 1226.

Table II. Yields of Products (KO_2 Reaction with 5a-e)

5	8, % yield (mp, °C)	9, % yield (mp, °C)	$ArCO_2H$ + $Ar'CO_2H$	$Ar'CO_2H$/ $ArCO_2H$
a	8.2 (169-174)	5.2 (202-204)	108	1.0[a]
b	10 (184-188)		107	5.25[b]
c[c]	8.7 (75-79)	17	93	1.63[a]
c		20 (230-234)	169	1.25
d	7.8 (205-206)	6.8 (226)	114	1.31[a]
e	7.2 (182-184)		179	2.25[a]

[a] Determined from ^1H NMR spectra in Me_2SO. [b] Determined from the IR bands at 855 and 715 cm^{-1} by plotting the ratio vs. % acid. [c] With bubbling O_2.

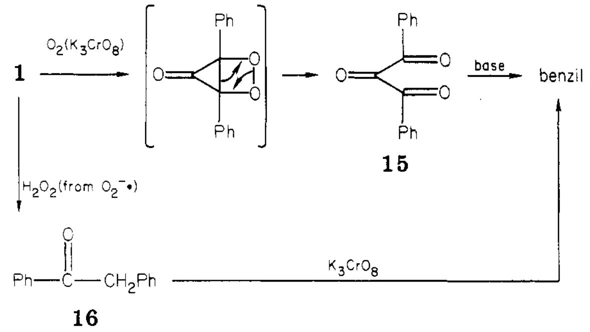
which does not involve electron transfer as the first step is also possible, producing benzil instead by dioxetane formation via **10**, **11**, and **12**. For the vinylogous case of tetracyclones Rosenthal showed that about 10% avoid electron transfer.



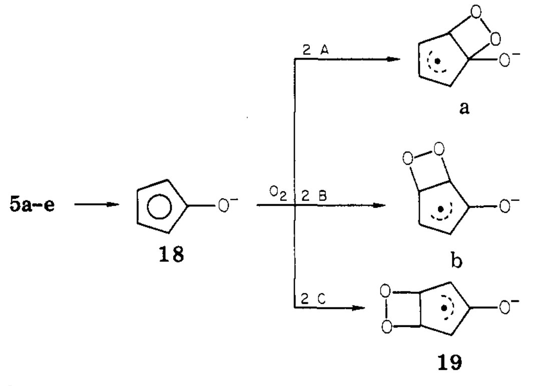
Qualitatively KO_2 reacts much more slowly with **1** than with **5** because reduction of **5** affords a Hückel stabilized radical anion whereas **1** leads to the anti-aromatic anion **9**.

The benzil formed does not derive from a slow thermal decarbonylation of **1**, giving diphenylacetylene (**17**), followed by oxidation. In a control experiment **17** was treated with KO_2 for one week. All starting materials were recovered intact after workup.

In contrast to the earlier report,[5] benzil is also not derived from the reaction of singlet oxygen with **1**. Since it is known that singlet oxygen can be produced from KO_2,[12] this possibility must be excluded. A solution of **1** in aqueous dioxane (55%) was irradiated for 9 h with a 500-W lamp ($\lambda > 400$ nm, $NaNO_2$ filter) in the presence of the classic singlet oxygen sensitizer—rose bengal. During this time two separate samples of 200 mg of rose bengal (used as the sensitizer) were bleached but 50% of **1** was recovered after chromatography of the dichloromethane extract. Because of the expected short half-life of singlet oxygen in aqueous dioxane[13] the photoreaction was repeated in benzene/carbon tetrachloride (4:1) with crown ether added to the solvent mixture to solubilize the rose bengal. The presence of singlet oxygen under these conditions was confirmed by addition of purple **5**, which was bleached by its known reaction[14] with singlet oxygen. The expected product **15** from the reaction of **1** with singlet oxygen, which we independently synthesized,[16] was shown absent in this control. This clearly indicates that, even though a substantial excess of singlet oxygen was generated under the conditions of the experiment, there is no reaction of **1** either in aqueous dioxane or in CCl_4/benzene. As shown below, the formation of benzil from **1** and K_3CrO_8[5] likely derives from desoxybenzoin (**16**) —the known hydrogen peroxide product from **1**[15] by reaction with H_2O_2, which is formed from KO_2 generated from K_3CrO_8.[17] K_3CrO_8 simply acts as an oxidizing species in transforming **16** to benzil.[18] There are also several theoretical considerations which explain the inertness of **1** towards singlet oxygen.[19] Thus tetraphenylcyclopropene chooses a polar addition[20] in which singlet oxygen acts as an electrophile. Our results support the contention of Peters et al.[17] that one should be cautious in attributing oxidations resulting from K_3CrO_8 to singlet oxygen.



The reaction of the cyclopentadienones **5a–e** with potassium superoxide is somewhat more complicated. Electron transfer from superoxide radical anion to **5** produces the tetracyclone radical anion **18**. Three nonidentical dioxetanes can be formed from **18**. It is likely that 2-pyrones are formed via intermediate **19a**. Oxidative opening of **19a**, via **20**, gives a reaction with KO_2/O_2 followed by ring closure to 2-pyrones **9a,c,d**.



The observed ratios of pyrones **9** to furanones **8** (Table II) favor this mechanism. Electron acceptor substituents in the 3 and 4 position of **4** increase the yield of **8** while electron-donating substituents in the 3 and 4 position enhance formation of **9**. The discriminative step is,

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(13) Merkel, P. B.; Kearns, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 1029.

(14) Foote, C. S.; Wexler, S. *J. Am. Chem. Soc.* **1974**, *86*, 3879.

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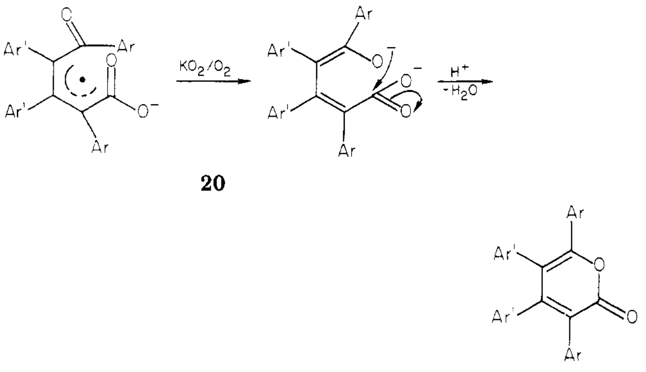
(16) Bigelow, L. A.; Hanslick, R. S. "Organic Synthesis"; Wiley: New York, 1943; Collect. Vol. 2, p 244.

(17) Peters, J. W.; Bekowies, P. J.; Winer, A. W.; Pitts, J. N. *J. Am. Chem. Soc.* **1975**, *97*, 3299.

(18) Hodgson, E. K.; Fridovich, I. *Biochemistry* **1974**, *13*, 3811.

(19) Frimer, A.; Antebi, A. *J. Org. Chem.* **1980**, *45*, 2334.

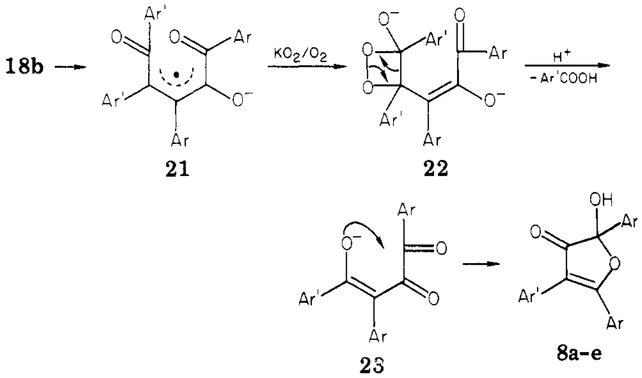
(20) Politzer, T. R.; Griffen, G. W. *Tetrahedron Lett.* **1973**, 4775.



20

9a,c,d

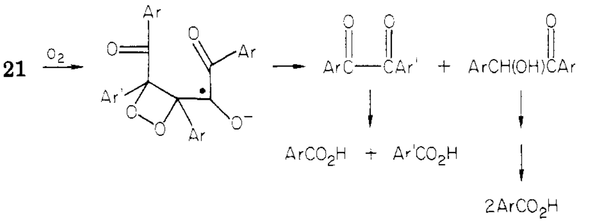
therefore, the reaction of molecular O_2 with the radical anion **18**. Higher electron density (*p*-anisyl or *p*-tolyl substituents) at the 3 and 4 positions of the cyclopentadienone ring favors reaction B which leads exclusively to furanones **8**, while lower electron density at the 3 and 4 position (*p*-chlorophenyl or phenyl) favors A and B. While **18a** yields exclusively pyrone **9**, **18b** can produce both **8** and **9**. In fact TLC showed that both **8** and **9** are formed from all tetracyclones **5a–e**. But the yields were low in the case of **9b** and **9e**. The ratio of acids ($Ar'CO_2H/Ar-CO_2H$) observed in Table II is also in agreement with this explanation.



21 **22**

23 **8a–e**

The formation of $ArCO_2H$ results assumedly from an oxidative degradation of **21**, for example, as follows:



The formation both of pyrone **9** and the furanone **8** requires 2 mol of KO_2. In one experiment the effect of a stream of dry oxygen on the KO_2 reaction of **5c** was studied. The yield of **8c** and consequently the acid ratio was increased (Table II), but the total yield of the acids was decreased.

Experimental Section

General Methods. Melting points were determined by using a Thomas Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 337 on KBr discs, UV spectra on a Beckman Acta IV spectrometer, and mass spectra on a Varian MAT CH7 spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer. Unless otherwise indicated, $CDCl_3$ is used as the solvent with tetramethylsilane as the internal standard, coupling constants (J) are in hertz, and chemical shifts are in δ values. Analytical TLC was performed on silica gel 78-F plates (J. T. Baker) and preparative chromatography was done by using silica gel (60–200 mesh, Baker).

Benzil was purchased from Eastman Kodak, and dicyclohexano-18-crown-6, dimethoxybenzil, dimethylbenzil, 1,3-diphenylacetone, 4-methoxyphenylacetic acid, *p*-chlorophenylacetic acid, and 4-chlorobenzaldehyde were purchased from Aldrich Chemical Company. Rose bengal (technical) was purchased from Eastman Kodak Co., and benzoic acid and diphenylacetylene were purchased from Aldrich Chemical Co. Diphenylcyclopropenone (**1**)[21] and diphenyl triketone[22] were prepared by literature procedures.

Preparation of Starting Materials. (a) *p,p'*-Dichlorobenzil. Thiamin hydrochloride 3.5 g (0.25 mol) was dissolved in 7 mL of water and 32 mL of ethanol (95%) and then cooled in an ice bath. NaOH (7 mL, 3 N) was added within 7 min. To this solution was added 27.5 g (0.20 mol) of *p*-chlorobenzaldehyde and the mixture was heated at 60 °C for 1.5 h. At this temperature the thiamin slowly dissolved. Then the reaction mixture was left at room temperature overnight and the precipitated crystals were filtered, washed with ice-cold 95% ethanol, and recrystallized from 100 mL of 95% ethanol to afford 0.50 g of yellow crystals of *p,p'*-dichlorobenzoin. The mother liquor contained *p,p'*-dichlorobenzoin, which was oxidized by $CuSO_4$/pyridine to give after recrystallization from carbon tetrachloride (500 mL) 14.5 g (21% yield) of *p,p'*-dichlorobenzil.

(b) 1,3-Bis(*p*-chlorophenyl)propan-2-one. *p*-Chlorophenylacetic acid (10 g, 0.059 mol) was neutralized with 3.3 g (0.06 mol) of CaO suspended in water. The mixture was dried overnight at 140 °C. Dry vacuum distilliation from a 50-mL flask with a Bunsen burner gave 4.51 g (72% yield) of crude product that was recrystallized from ethanol (95%) to give white crystals of 1,3-bis(*p*-chlorophenyl)propan-2-one, mp 84 °C.

(c) 1,3-Bis(*p*-methoxyphenyl)propan-2-one. *p*-Methoxyphenylacetic acid (9.81 g, 0.059 mol) was neutralized with 3.3 g (0.06 mol) of CaO suspended in water. The mixture was dried overnight at 140 °C. Dry distillation in vacuo yielded 0.50 g (3.6%) of 1,3-bis(*p*-methoxyphenyl)propan-2-one after recrystallization from ethanol (absolute) as colorless crystals, mp 80–82 °C.

General Procedures for the Reactions with KO_2/Crown Ether. To a benzene solution (50 mL) containing the substrate and dicyclohexano-18-crown-6 is added at room temperature 1 equiv of powdered KO_2; the solution is then stirred and protected from light and moisture. After 48 h a second equivalent of KO_2 is added. Stirring is continued for 5 days more. The mixture is then poured into 50 mL of water and 50 mL of ether is added. After a second ether extraction, the two ether extracts (50 mL each) are combined and dried over Na_2SO_4. The solvent is evaporated and the residue chromatographed with CH_2Cl_2. The aqueous layer is acidified with 1 N HCl until pH 1 and extracted with ether (first 100 mL then 2 × 50 mL), the combined ether extracts are dried, and evaporation of the solvent affords the acid.

(a) Reaction with Diphenylcyclopropenone (1). From 0.581 g (2.82 mmol) of **1**, 0.500 g (2.69 mmol) of dicyclohexano-18-crown-6, and 0.382 g (5.37 mmol) of KO_2, was obtained 90 mg (18%, yield based on reacted **1**) of benzil (IR (KBr) and mass spectra identical with those of an authentic sample), mp 87–92 °C (lit. 94–95 °C), from a first yellow fraction. Then acetone (5%) was added to the eluent and 82 mg (14%, yield) of unreacted diphenylcyclopropenone (**1**) were eluted. From the aqueous layer was obtained 81 mg of slightly yellow crystals (27%, yield) of benzoic acid, mp 115–117 °C (lit. 122–123 °C).

(b) Reaction with Tetracyclone 5a. From 1.073 g (2.5 mmol) of **5a**, 0.50 g (1.34 mmol) of dicyclohexano-18-crown-6, and 0.278 g (3.9 mmol) of KO_2 in 100 mL of benzene was obtained 363 mg of colorless crystals from the acidified layer. The ^1H NMR spectrum in Me_2SO reveals this to be a 1:1 mixture of benzoic and *p*-toluic acids (108% total yield). Three different fractions were eluted from the column. The first fraction afforded 298 mg of yellowish crystals which were not identified. The mass spectrum exhibited a molecular ion at *m/e* 238 (isomer of dimethylbenzil). The second fraction afforded 58 mg of slightly yellow crystals of 3,6-diphenyl-4,5-di-*p*-tolylpyran-2-one (**9a**), mp 190–196 °C (lit.[23]

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[21] Deen, M. L. *Synthesis* **1972**, 675.

[22] Fieser, L. F.; Haddadin, M. J. *Can. J. Chem.* **1965**, *43*, 1599.

[23] Ho, T.; Hall, T. W.; Wong, C. M. *Synth. Commun.* **1979**, *3*, 79.

198–200 °C); IR (KBr) 3025 w, 2920 m, 1725 ss, 1625 w, 1451 m, 1355 w, 1235 m, 1155 w, 1098 s, 1045 w, 1020 w, 930 s, 906 ss, 755 m, and 700 s cm^{-1}; UV λ_{max} (CH_3CN) 337 nm (ε 12 300); ^1H NMR ($CDCl_3$) δ 2.13 and 2.21 (s, 6 H, CH_3), 6.63, 6.70, 6.76, 6.81, 7.13, 7.25 (aromatic H); ^{13}C NMR ($CDCl_3$) (cf. lit.[24]) 21.20 and 29.75 (CH_3), 119.77, 125.08-136.9 (6 aromatic H), 155.66, 156.49, 162 (C=O); mass spectrum, *m/e* (relative intensity) 428 (31) 400 (100), 357 (24), 295 (97). The last fraction afforded 73 mg (8.2% yield) of colorless crystals with the typical "snake-like" appearance of 2-hydroxy-2,4-diphenyl-5-*p*-tolylfuran-3-one (**8a**), mp 169–174 °C; IR (KBr) 3260 w (OH), 1690 s, 1615 ss, 1585 m, 1495 w, 1460 w, 1230 s, 1095 s, 905 ss, 700 s cm^{-1}; UV λ_{max} (CH_2Cl_2) 327 nm; ^1H NMR ($CDCl_3$) δ 2.40 (s, CH_3), 3.57 (s, OH), 7.0–7.7 (aromatic H); mass spectrum, *m/e* (relative intensity) 342 (7), 326 (21), 314 (10), 337 (100).

(c) Reaction with Tetracyclone 5b. From 1.00 g (2.13 mmol) of **4b**, 0.50 g (1.34 mmol) of dicyclohexano-18-crown-6, and 250 mg (3.51 mmol) of KO_2 in 40 mL of benzene was obtained 0.343 g of colorless crystals from the acid extract. The IR spectrum shows them to be a mixture of *p*-chlorobenzoic acid and benzoic acid (107%, total yield). The last fraction from the column affords 75 mg (10%, yield) of colorless crystals of 2-hydroxy-2,4-diphenyl-5,6-chlorophenyl)furan-3-one (**8b**), mp 184–188 °C); IR (KBr) 3250 w (OH), 2975 w, 2925 w, 1705 s, 1685 s, 1620 s, 1600 s, 1480 m, 1420 m, 1380 m, 1235 s, 1095 ss, 900 ss (br), 700 w cm^{-1}; UV λ_{max} (CH_2Cl_2) 330 nm (ε 16 500); ^1H NMR ($CDCl_3$) δ 4.15 (s, OH), 7.15–7.80 (aromatic H); mass spectrum, *m/e* (relative intensity) 362 (6), 346 (8), 334 (9), 257 (71), 139 (53), 105 (100).

(d) Reaction with Tetracyclone 5c in an Oxygen Stream. From 1.16 g (2.6 mmol) of **4c**, 0.50 g (1.34 mmol) of dicyclohexano-18-crown-6 in 80 mL of benzene, and 280 mg (3.9 mmol) of KO_2 was obtained 340 mg of slightly yellow crystals from the acid extract. The ^1H NMR spectrum revealed them to be a 1.6:1 mixture of *p*-methoxybenzoic acid and benzoic acid (93%, total yield). The first fraction from the column afforded 206 mg (17%, yield) of slightly yellow crystals of 3,6-diphenyl-4,5-bis(*p*-methoxyphenyl)pyran-2-one (**9c**), mp 234 °C; IR (KBr) 2950 w, 2920 w, 2320 w, 1705 ss br, 1605 m, 1510 s, 1445 w, 1385 m, 1340 s, 1283 s, 1238 ss, 1020 s, 750 br m, 702 s cm^{-1}; UV λ_{max} (CH_2Cl_2) 342 nm (ε 18 100); ^1H NMR ($CDCl_3$) δ 3.65 and 3.71 (s, CH_3), 6.52, 6.58, 6.64, 6.71, 7.05–7.35 (aromatic H); mass spectrum, *m/e* (relative intensity) 460 (36), 432 (100), 327 (86). A second fraction yielded 82 mg (8.7%) of colorless 2-hydroxy-2,4-diphenyl-5-(*p*-methoxyphenyl)furan-3-one (**8c**), mp 80–85 °C; IR (KBr) 3240 w, 2920 w, 1750 w, 1700 br s, 1605 br ss, 1570 w, 1520 m, 1690 w, 1390 m, 1250 ss, 1170 s, 1095 s, 1025 m, 900 s, 840 m, 700 m cm^{-1}; UV λ_{max} (CH_2Cl_2) 336 nm; ^1H NMR ($CDCl_3$) δ 3.63 (s, OH), 3.88 (s, CH_3), 6.89, 7.00, 7.25, 7.50, 7.99, 8.01, 8.03, 8.10, 8.12 (aromatic H); mass spectrum, *m/e* (relative intensity) 362 (6), 342 (85), 330 (100), 253, 135, 105.

(e) Reaction with Tetracyclone 5d. From 150 mg (0.292 mmol) of **5d**, 97.5 mg (0.3 mmol) of dicyclohexano-18-crown-6, and 34.4 mg (1.65 equiv) of KO_2 in 8 mL of benzene was obtained 52.3 mg of colorless crystals from the acid extract. The ^1H NMR spectrum in Me_2SO revealed them to be a mixture (1:1.31) of *p*-chlorobenzoic acid and *p*-methoxybenzoic acid (114%, total yield). A first fraction afforded 10.5 mg (yield,6.8%) of slightly yellow 3,6-bis(*p*-chlorophenyl)-4, 5-bis(*p*-methoxyphenyl)pyran-2-one (**9d**), mp 225–226 °C. With additional 5% acetone a second fraction was obtained yielding 9.5 mg (7.2%, yield) of colorless 2-hydroxy-2,4-bis(*p*-chlorophenyl)-5-(*p*-methoxyphenyl)furan-3-one (**8d**), mp 205–206 °C; IR (KBr) 2975 w, 2925 w, 1705 s, 1680 m, 1380 s, 1260 m, 1235 m, 1095 ss, 900 ss, 635 w cm^{-1}; UV λ_{max} (CH_2Cl_2) 343 nm; ^1H NMR ($CDCl_3$) δ 3.65 (s, CH_3), 3.88 (s, CH_3), 6.89, 7.00, 7.25, 7.39, 7.50, 7.99, 8.01, 8.10, 8.12 (aromatic H); mass spectrum, *m/e* (relative intensity) 426 (1.3), 410 (4.5), 398 (1.8), 287 (11), 135 (100).

(f) Reaction with Tetracyclone 5e. From 0.25 g (0.487 mmol) of **5e**, 0.189 g (0.487 mmol) of dicyclohexano-18-crown-6, and 38.1 mg (1.1 equiv) of KO_2 in 10 mL of benzene was obtained 135 mg of colorless crystals from the acid extract. The ^1H NMR spectrum revealed them to be a 9:4 mixture of *p*-chlorobenzoic acid and *p*-methoxybenzoic acid (179%, total yield). Column chromatography yielded 14.9 mg (7.2%, yield) of yellowish crystals of 2-hydroxy-2,4-bis(*p*-methoxyphenyl)-5-(*p*-chlorophenyl)furan-3-one (**8e**), mp 182–184 °C; IR (KBr) 3240 w, 2910 w, 1680 s, 1610 m, 1600 m, 1510 m, 1245 s, 1230 s, 1095 ss, 935 ss, 900 br ss, 840 m cm^{-1}; UV λ_{max} (CH_2Cl_2) 343 nm (ε 5 200); ^1H NMR ($CDCl_3$) δ 3.70 (s, OH), 3.78 (s, CH_3), 6.8–7.8 (aromatic H); mass spectrum, *m/e* (relative intensity) 422 (5), 406 (6.5), 394 (2.5), 287 (100).

(g) Reaction with Diphenylacetylene. From 0.80 g (4.49 mmol) of diphenylacetylene, 0.30 g (0.18 equiv) of dicyclohexano-18-crown-6, and 480 mg (1.5 equiv) of KO_2 the workup afforded only the unchanged diphenylacetylene.

Reaction of 1 in Aqueous Dioxane. To a vigorously stirred solution of 0.103 g (0.5 mmol) of **1** in 10 mL of aqueous dioxane (55%) was added in small portions 100 mg (1.6 mmol) of KO_2. The color changed spontaneously to orange. Stirring was continued for $^1/_2$ h. Then 50 mL of water and 100 mL of CH_2Cl_2 were added and the combined organic layers extracted. Two more extractions with 50 mL of CH_2Cl_2 were completed. Washing of the CH_2Cl_2 phase three times with 50 mL of water, drying the organic layer over Na_2SO_4, and evaporation of the solvent afforded traces of a mixture of products that were identified on TLC with the products from H_2O_2/NaOH and **1**. Acidification of the aqueous layer with 1 N HCl and extraction with 50 mL of ether (three times) afforded 35 mg (57%, yield) of benzoic acid containing traces of desoxybenzoin (detected by ^1H NMR).

Dye-Sensitized Photooxidation of 1 in Benzene/CCl_4. A solution of 0.40 g (1.94 mmol) of **1**, 0.15 g (1.5×10^{-4} M) of rose bengal and 0.35 g (0.94 mmol) of dicyclohexano-18-crown-6 in 280 mL of benzene/CCl_4 (4:1) was irradiated in an 300-mL immersion photoreactor (Pyrex) with a 500-W lamp (General Electric A 500T 3/Cl). The reactor was equipped with a gas inlet tube (fritted ball) and a magnetic stirring bar. Saturated $NaNO_2$ solution was used as a filter ($\lambda > 400$ nm). After 1 h of irradiation, during which the solution was stirred and purged by a stream of dried oxygen, the rose bengal was bleached and additional an 0.15 g of rose bengal together with 0.20 g of **4** were added to the photolysate. Irradiation was continued for 2 h more during which the solution became decolorized. Comparison of the photolysate by TLC (CH_2Cl_2 as eluant) with benzil and diphenyltriketone showed that the only new product was dibenzoylstilbene (the photoproduct from tetracyclone **4**) and traces of diphenylacetylene (the photoproduct from **1**).

Dye-Sensitized Photooxidation of 1 in Aqueous Dioxane (55%). A solution of 0.80 g (3.88 mmol) of **1** and 0.254 g (2.5×10^{-4} M) of rose bengal in 280 mL of aqueous dioxane (55%) was irradiated as in benzene. Rose bengal was bleached after 4.5 h, and an additional 254 mg of rose bengal was bleached after 4 h more. To the photolysate were added 200 mL of water and 200 mL of CH_2Cl_2 and the organic phase was extracted. After 2 more extractions with 100 mL of CH_2Cl_2 each, the organic layer was washed twice with 100 mL of water and dried over Na_2SO_4. The solvent was removed and the residue was chromatographed with CH_2Cl_2/acetone (10:1). Nothing was evident except **2**.

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Registry No. **1**, 886-38-4; **5a**, 38305-61-2; **5b**, 38268-08-5; **5c**, 668-29-1; **5d**, 87411-85-6; **5e**, 87411-86-7; **8a**, 87411-87-8; **8b**, 87411-88-9; **8c**, 87411-89-0; **8d**, 87411-90-3; **8e**, 87411-91-4; **9a**, 40938-59-8; **9c**, 87411-92-5; **9d**, 87411-93-6; KO_2, 12030-88-5; rose bengal, 11121-48-5; *p,p'*-dichlorobenzil, 3457-46-3; *p*-chlorobenzaldehyde, 104-88-1; *p*-chlorophenylacetic acid, 1878-66-6; *p*-methoxyphenylacetic acid, 104-01-8; 1,3-bis(*p*-chlorophenyl)propan-2-one, 65622-34-6; 1,3-bis(*p*-methoxyphenyl)propan-2-one, 29903-09-1.

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(24) C=O of 2-pyrone; 162.0 ppm; Turner, W. V.; Pirkle, W. H. *J. Org. Chem.* **1974**, *39*, 1935.