J. Org. Chem. 1984, 49, 3340–3344

of the molecule. Like Makriyannis and Knittel,[19] we have found[5] that aromatic methoxyls with only one ortho substituent have ^{13}C NMR chemical shifts of 56.0 ± 0.5 ppm whereas 3,4,5-trimethoxybenzene derivatives have one resonance (presumably the 4-methoxyl carbon) at approximately δ 60. This may be attributable to an out-of-plane, nonconjugated conformation. In compound 1, the methoxyl shifts are δ 55.5 and 55.9.

Finally, it is interesting to comment on the resistance of the 10-hydroxyl group of compounds such as 1 to acetylation, even under forcing conditions, and the failure[1] to prepare the 10-OMe analogue from 10-methoxyanthrone (oxanthrone methyl ether, 9-oxo-10-methoxydihydroanthracene) and the appropriate γ-methyl or γ-hydroxymethyl quinone methide. A space-filing representation, Figure 5, indicates the inaccessibility of the H-bonded 10-OH in this rather rigid structure.

In summary, it has been demonstrated that proton NMR gives detailed insight into the solution conformation of compounds such as 1. In these compounds, the conformations in solution clearly resemble the solid-state structure and it has been shown that the most stable rotamer in solution is the sole conformer observed in the solid state.

Experimental Section

The preparation and full spectral details of compounds 1–5 have been reported previously.[1-5]

Proton NMR spectra were determined in $CDCl_3$ or acetone-d_6 on a Bruker WH270 FT spectrometer, with tetramethylsilane as internal reference. Temperature measurements to ±0.1 °C were made by inserting an NMR tube containing solvent and a thermocouple into the probe and measuring the equilibrium temperature before and after a spectrum was recorded.

Crystal and Molecular Structure of $C_{33}H_{30}O_7$. A colorless plate-like crystal of dimensions 0.25 × 0.225 × 0.07 mm was obtained by slow diffusion of pentane through a porous clay disk (from a flower pot) into a solution of 1 in acetone. Preliminary precession photography indicated the triclinic crystal class. Lattice parameters were obtained from the setting angles of 25 reflections centered on an Enraf-Nonius CAD4 diffractometer using Cu K_α X-rays. Details are available as supplementary material.

Acknowledgment. We thank Dr. T. Jones, University of Auckland, for collection of the X-ray data, and Dr. Bruce Adams, University of Wisconsin—Madison, for his input to the VT NMR work. This work was done in part while John Ralph was a PhD candidate at the University of Wisconsin—Madison, and partial funding by the New Zealand Advisory Council is gratefully acknowledged.

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Supplementary Material Available: Details of the crystal data solution and refinement, tables of positional parameters, bond lengths, and angles, thermal parameters, and coordinates of calculated hydrogen positions (8 pages). Ordering information is given on any current masthead page.

Oxidatively Catalyzed Nucleophilic Aromatic Substitution. Further Studies on the $S_{ON}2$ Reaction

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The oxidation of several electron-rich fluoroarenes in the presence of a nucleophile, usually acetate ion, has been investigated. Two substrates, 1- and 2-fluoronaphthalene, have been shown to undergo a formally nonoxidative fluorine/acetoxy exchange induced by chemical oxidants such as benzoyl peroxide, potassium peroxydisulfate, and copper(III). The mechanism is believed to involve electron-transfer chain catalysis according to the $S_{ON}2$ mechanism. On electrochemical oxidation of these substrates, the major reaction pathway observed was oxidative substitution of hydrogen. The catalytic efficiency of the anodically initiated title reaction is also improved at higher temperatures; e.g., anodic acetoxydefluorination of 4-fluoroanisole takes place with a current efficiency of 590% at 78 °C. We also give the first example of an intramolecular although not catalytic $S_{ON}2$ reaction.

Electron-transfer reactions involving radical ion intermediates are becoming increasingly important when considering organic reaction mechanisms. One class of this type of reactions is electron-transfer chain (ETC) reactions,[1] i.e., initiation by reductants or oxidants. The $S_{RN}1$ reaction[2] is a well-known example of a reductively initiated reaction and, on the oxidative side, catalyzed cycloaddition reactions[3] provide entries into hitherto unrealized transformations.

We have recently studied oxidatively induced nucleophilic substitutions on aromatic halides, another possible class of ETC reactions. The first example of this formally redox neutral reaction was discovered by us in 1976;[4] oxidation of 4-fluoroanisole in the presence of acetate ion gave 4-acetoxyanisole.

In 1980, Alder[5] proposed the existence of the $S_{ON}2$ mechanism:

$$\text{Ar–X} \xrightarrow{-e} (\text{Ar–X})^{+\cdot} \qquad \text{initiation} \tag{1}$$

$$(\text{Ar–X})^{+\cdot} + \text{Nu}^- \rightarrow (\text{X–Ar–Nu})\cdot \xrightarrow{-X^-} (\text{Ar–Nu})^{+\cdot} \tag{2}$$

$$(\text{Ar–Nu})^{+\cdot} + \text{ArX} \rightleftharpoons \text{Ar–Nu} + (\text{Ar–X})^{+\cdot} \quad \text{propagation} \tag{3}$$

Evidence for the participation of this mechanism in the

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[1] For a review of electron-transfer catalyzed reactions, see: Eberson, L. *J. Mol. Catal.* **1983**, *20*, 27.

[2] Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.

[3] (a) Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133. (b) Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1982**, *104*, 2665.

[4] Nyberg, K.; Wistrand, L.-G. *J. Chem. Soc., Chem. Commun.* **1976**, 898.

[5] Alder, R. W. *J. Chem. Soc., Chem. Commun.* **1980**, 1184.

0022-3263/84/1949-3340$01.50/0

Table I. Oxidation of Fluoronaphthalenes in HOAc/0.5 M KOAc[a]

entry	substrate	oxidant	temperature, °C	products, (yield, %)[b]
1	1	anode	20	**1a** (1.2) **1c** (28)
2	1	BPO	78	**1a** (140) **1b** (5.8)
3	1	BPO[c]	78	**1a** (60) **1b** (7.4)
4	1	$K_2S_2O_8$	110	**1a** (18)[d]
5	1	$K_2S_2O_8$[e]	110	**1a** (58)[d]
6	1	Cu(III)[f]	110	**1a** (80)[d]
7	1	Cu(III)[f,g]	110	**1a** (28)[d]
8	2	anode	20	**2a** (0.71)[h]
9	2	BPO	78	**2a** (16) **2b** (0.93)
10	2	$K_2S_2O_8$	110	**2a** (8)[f]

[a] For conditions, see Experimental section. [b] The yields were determined by GLC with internal standards and are based on no catalytic cycles, i.e., 1 molecule of **1a** and **2a** formed respectively for each radical. In the anodic cases, the yields of **1a** and **2a** respectively are based on a one-electron process, and the yield of **1c** is based on a two-electron process. [c] In the presence of an equimolar amount (to BPO) of Cu(II). [d] Small amounts (<1%) of normal substitution products were formed in these reactions. [e] In the presence of 10% (to $K_2S_2O_8$) of Cu(II). [f] The biuret complex of Cu(III) was used.[6] [g] In the presence of a 4-fold excess of Cu(II) (to Cu(III)). [h] The major products were two isomeric fluoroacetoxynaphthalenes (identified only by mass spectrometry) in a total yield of around 30%.

oxidation of 4-fluoroanisole was then presented by us.[6] At the same time, another entry into the $S_{ON}2$ reaction, initiated by benzoyloxy radicals was found:[7]

$$\text{Ar–X} + \text{PhCOO}^{\cdot} \rightarrow (\text{X–Ar–OOCPh})\cdot \text{ initiation} \quad (4)$$

$$(\text{X–Ar–OOCPh})\cdot \xrightarrow{-\text{X}^-} (\text{Ar–OOCPh})^{+\cdot} \quad (5)$$

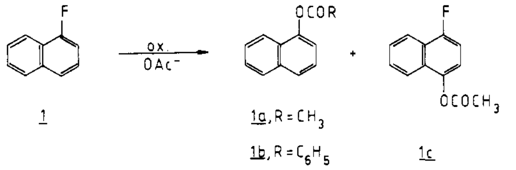
$$(\text{ArOOCPh})^{+\cdot} + \text{Ar–X} \rightleftharpoons \text{Ar–OOCPh} + (\text{Ar–X})^{+\cdot} \text{ propagation} \quad (6)$$

$$(\text{ArX})^{+\cdot} + \text{Nu}^- \rightarrow \rightarrow (\text{ArNu})^{+\cdot} + \text{X}^- \quad (7)$$

Although a number of aromatic halides were found to undergo metal ion (especially Cu(III)) induced solvolysis[6] via the $S_{ON}2$ mechanism, the anodically initiated reaction remained an almost singular case. We now present further results on the scope and mechanism of the $S_{ON}2$ reaction with special regard to electrochemical and benzoyloxy radical initiation.

Results

Oxidation of Fluoronaphthalenes. In an earlier paper,[6b] we mentioned a number of substrates that did not undergo the $S_{ON}2$ reaction, among them 1-fluoronaphthalene (**1**). A more careful analysis of the products



(8)

from anodic oxidation of this substrate in HOAc/0.5 M KOAc revealed, however, that a small amount of 1-acetoxynaphthalene (**1a**) was formed together with the

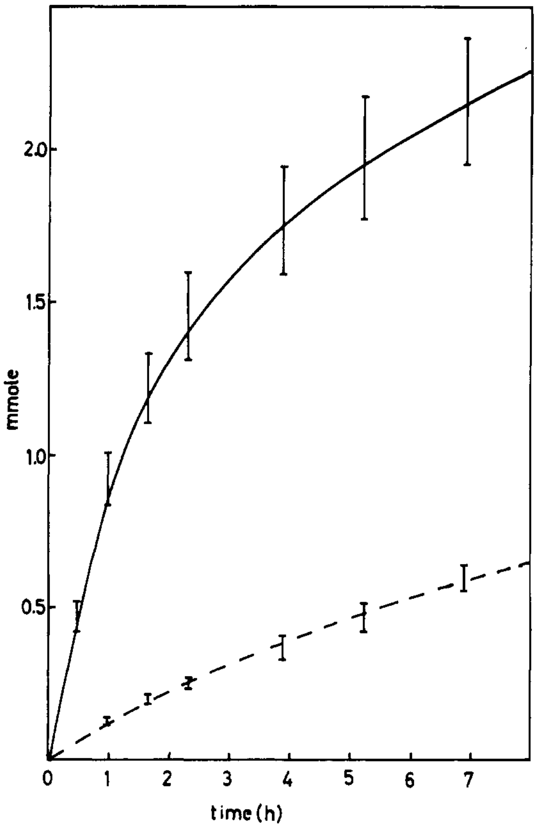


Figure 1. Formation of **1a** (—) and consumed BPO (--) vs. time, in the reaction between BPO (1 mmol) and **1** (10 mmol) in HOAc/0.5 M KOAc at 78 °C.

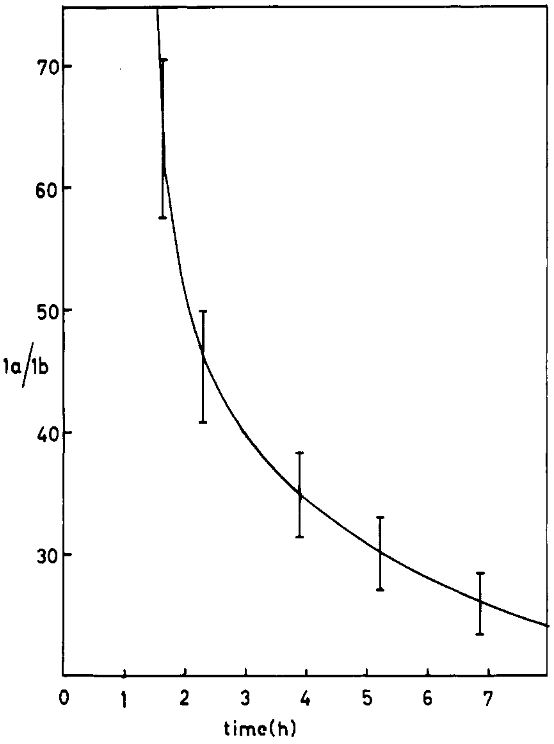


Figure 2. Ratio of **1a** to **1b** vs. time in the decomposition of BPO in the presence of **1** in HOAc/0.5 M KOAc at 78 °C.

"normal" substitution product **1c** (Table I, entry 1). A thorough investigation of this substrate was therefore undertaken. A more successful acyloxydefluorination was induced by benzoyl peroxide (BPO) as initiator in HOAc containing 0.5 M KOAc, where a high yield of **1a** was observed (Table I, entry 2). The ratio of **1a** to **1b** was 24

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(6) (a) Eberson, L.; Jönsson, L. *J. Chem. Soc., Chem. Commun.* **1980**, 1187. (b) Eberson, L.; Jönsson, L.; Wistrand, L.-G. *Tetrahedron* **1982**, *38*, 1087.

(7) Eberson, L.; Jönsson, L. *J. Chem. Soc., Chem. Commun.* **1981**, 133.

Table II. Anodic Oxidation of Fluoroaromatics in HOAc/0.5 M KOAc[a] at Different Temperatures

entry	substrate	temperature, °C	products (yield, %)[b]
1	1	20	**1a** (1.2) **1c** (28)
2	1	78	**1a** (28) **1c** (29)
3	1	100	**1a** (16) **1c** (30)
4	2	20	**2a** (0.7)[c]
5	2	78	**2a** (3.6)[c]
6	3	20	4-acetoxyanisole (270)[d]
7	3	78	4-acetoxyanisole (590)
8	3	100	4-acetoxyanisole (440)
9	4	20	2-acetoxyanisole (59)
10	4	78	2-acetoxyanisole (120)

[a] For conditions, see Experimental Section. The reactions were run to a conversion of 2% based on a one-electron process. [b] Based on a one-electron process. [c] The major products were two different fluoroacetoxynaphthalenes (identified by mass spectrometry); total yield around 30%. [d] From ref 6.

corresponding to an average of 24 cycles initiated for every benzoyloxy radical attack ipso to the fluorine. A detailed analysis of this reaction is shown in Figure 1 where the yield of **1a** and the consumption of BPO is plotted against time. The efficiency of the process is highest at low conversion of BPO and the maximum yield can be calculated to be as high as 370%.[8] The same effect can also be seen in Figure 2 where the **1a**/**1b** ratio is plotted against time. The number of cycles initiated by the benzoyloxy radical is very high in the early stages of the reaction and decreases slowly to reach the number observed after completion of the reaction.

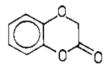
Anodic oxidation of 2-fluoronaphthalene (**2**) in HOAc/0.5 M KOAc gave a small amount of the product from ipso substitution, 2-acetoxynaphthalene (**2a**), together with two unidentified "normal" substitution products (Table I, entry 8). In the reaction of **2** with BPO the same effect as for **1** was observed (Table I, entry 9), a much more efficient acyloxydefluorination than when using the anode as initiator. Especially noteworthy is the fact that the number of catalytic cycles induced by BPO is comparable for the two substrates, **1** and **2** (24 and 17, respectively).

Acyloxydefluorination of fluoronaphthalenes was also induced by peroxydisulfate (Table I, entries 4 and 10). In order to catalyze the decomposition of peroxydisulfate to $SO_4^{-}\cdot$ we also ran an experiment in the presence of copper(II),[9] which gave a higher yield of **1a** (Table I, entry 5).

In earlier papers[6] we mentioned that copper(III) initiated hydrolysis of chloro- and fluorobenzenes under mild conditions (refluxing CF_3COOH/H_2O). We now show that copper(III) also catalyzes acyloxy defluorination of fluoronaphthalenes in acetic acid/acetate (Table I, entries 6 and 7).

Temperature Effect. In order to compare the efficiency of the anodic acetoxylation with substitution induced by BPO, **1** was oxidized electrochemically at 78 °C under otherwise identical conditions (Table II, entry 1). A substantial increase in the yield of **1a** was observed, whereas the yield of **1c** remained unchanged. A similar effect was observed on anodic oxidation of **2**, although on a more modest scale (Table II, entry 5). No further increase was observed on oxidation of **1** and **2** at 100 °C. This prompted us to reinvestigate the reported cases of anodically induced acetoxy defluorination, i.e., 4-fluoroanisole (**3**) and 2-fluoroanisole (**4**). As can be seen from Table II, entries 6–10, the trend is the same for these substrates. The most pronounced effect is on the anodic oxidation of 4-fluoroanisole, where the average chain length was more than doubled to 5.9.

Intramolecular Substitution. The possibility of an intramolecular acyloxydefluorination, an $S_{ON}i$ reaction, has been investigated. One candidate for this type of reaction is 2-fluorophenoxyacetic acid where the lactone **5** is the expected product of an $S_{ON}i$ reaction. However, on oxidation of this substrate electrochemically, with BPO or with potassium peroxydisulfate, no **5** was formed, only products derived from decarboxylation being observed.



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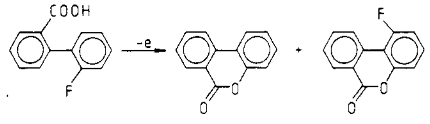
Another substrate which could be expected to undergo an intramolecular substitution reaction is the carboxylic acid **6**. This supposition is based on the fact, that on anodic oxidation the corresponding unfluorinated compound, biphenyl-2-carboxylic acid, is known to react preferentially intramolecularly to give the lactone **7**.[10] In our hands, anodic oxidation of **6** at 78 °C gave two neutral products, the expected lactone **7** (22%) accompanied by the "normal" substitution product **8** (3%).



6 7 8 (9)

Oxidation of **6** with $K_2S_2O_8$ also gave **7** (22%) and **8** (0.1%). As reference reactions we have also oxidized biphenyl-2-carboxylic acid with $K_2S_2O_8$ and $K_2S_2O_8$/Cu(II) (10:1) and this gave in the first case biphenyl (88%) and **7** (12%) and in the second case **7** (77%) and biphenyl (3%).

Reaction of **6** with BPO gave on the other hand no neutral products.

Discussion

The results presented on the oxidation of fluoronaphthalenes are in agreement with the proposed ETC mechanism outlined in eq 1–7, especially on initiation with BPO where a clean fluorine/acyloxy exchange takes place. However, anodic oxidation of these substrates preferentially gave products from oxidative substitution. What then, is the difference between these two methods of initiation? Electrochemical oxidation is, at least partly, a heterogeneous process where electrochemical and fast chemical steps occur in the electrochemical double layer. Moreover, the oxidative power of the anode (the applied potential on oxidation of **1** and **2** was roughly 2.0 V vs. SCE) is much higher than that of BPO (estimated $E°$ = 0.1 V vs. NHE[11]).

The chain-terminating step in the anodic initiation is presumably the formation of an oxidatively substituted product, since this is a major product:

$$(ArH)^{+\cdot} \xrightarrow{OAc^-} (H\text{-}Ar\text{-}OAc)\cdot \xrightarrow[-H^+]{-e} ArOAc \qquad (10)$$

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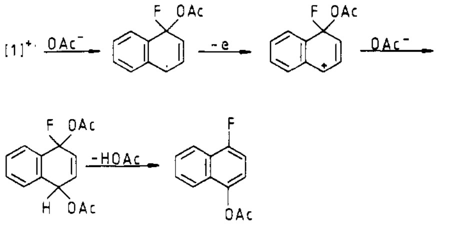
[8] The yield of **1a** and the ratio of **1a**/**1b** are seemingly contradictory. However, the yield of **1a** is somewhat arbitrarily based on a chain length of 1, i.e., 100% equals 2 molecules of **1a** for every BPO consumed. Since the benzoyloxylation of **1** is inefficient, the yield of **1a** is lowered accordingly.

[9] Jönsson, L.; Wistrand, L.-G. *J. Chem. Soc., Perkin Trans. 1* **1979**, 669.

[10] Eberson, L.; Nyberg, K. *J. Am. Chem. Soc.* **1966**, *88*, 1686.

[11] Eberson, L. *Adv. Phys. Org. Chem.* **1981**, *18*, 79.

This reaction requires an oxidant in the second step, and, in the anodic case, the potential applied is sufficient to oxidize the intermediate cyclohexadienyl radical if this species is close to the anode. Another possible termination step in the anodic initiation is further oxidation of the cyclohexadienyl radical, formed by ipso attack of acetate ion on the radical cation of 1 (eq 11). The resulting cation cannot eliminate a proton as in eq 10, but can instead be attacked by acetate ion; elimination of acetic acid then gives **1c**. We believe, that on initiation with BPO these oxidative steps are very slow, thus making the chain propagation longer before termination. This is in agreement with the retarding effect of Cu(II) on initiation with BPO and Cu(III),[12] since the oxidation required for an oxidative substitution should be feasible with this ion.



(11)

Thus, if in the anodic case the termination reaction occurs close to the anode, the ETC reaction must also take place here. This, in turn, suggests that the ETC reaction is very fast, being to a large extent terminated before diffusion from the electrode. This conclusion is supported by the observed temperature effect; by increasing the temperature, the diffusion rate is increased thereby allowing a higher fraction of reactive intermediates to diffuse into the bulk of the solution to continue the chain propagation undisturbed by the anode.

The same argument holds for 4-fluoroanisole, in this case, however, one must assume slower chemical reactions, thereby allowing a larger fraction of reactive intermediates to diffuse into the bulk of the solution. A significant observation in this context is the similarity in the number of cycles initiated by the anode at 78 °C (5.7) and by decomposition of BPO at the same temperature (5–8).[7] This indicates that, for the anodic initiation, most of the chemical reactions take place after diffusion from the anode.

Initiation with potassium peroxydisulfate is a somewhat intermediate case. The reactive species, the sulfate anion radical, is a powerful oxidant capable of oxidizing electron rich arenes,[9,13] but also a radical, and, thus, radical initiation according to eq 4–7 cannot be excluded.

The situation in the intramolecular reaction is also somewhat ambiguous. Earlier work on oxidation of aromatic carboxylic acids has shown that two different mechanisms can operate:[14]

$$\mathrm{ArCOOH} \xrightarrow{-e} (\mathrm{ArCOOH})^{+\cdot} \qquad (12)$$

$$\mathrm{ArCOO}^{-} \xrightarrow{-e} \mathrm{ArCOO}^{\cdot} \qquad (13)$$

In our case, the reactions were performed in a medium where both carboxylic acid and carboxylate are present, so both the oxidation of the aromatic moiety as outlined in eq 12 (pseudo-Kolbe reaction) and the Kolbe type oxidation in eq 13 are possible, and both would lead to an $S_{ON}i$ reaction. The pseudo-Kolbe reaction would provide an entry into the catalytic cycle via eq 1–3, and the Kolbe oxidation would give an intramolecular radical reaction analogous to eq 4–7.

In conclusion, we have shown that the success of the electrochemically induced $S_{ON}2$ reaction is highly dependent upon the stability of the intermediates, probably the radical cations and thus, easily oxidized substrates should be more inclined to undergo this type of reaction. This conclusion has also been reached by thermochemical calculations.[6] In addition, the reactions initiated by BPO should be more general since the outcome is not dependent upon heterogeneous reactions and there are no oxidative substitution reactions competing.

Experimental Section

General Methods. GLC analysis was carried out by using a Varian 1400 chromatograph equipped with an electronic integrator (HP 3380A) with either a 5% NPGS column (2 m × 3 mm) or a 5% OV-351 column (1 m × 3 mm). Proton nuclear magnetic resonance spectra were recorded on a Nicolet 360 MHz instrument. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane (δ units). Mass spectral analysis was carried out on a Finnigan 4021 spectrometer at 70 eV with a GLC inlet.

Materials. All materials were of highest commercial purity. The fluoro compounds used were purified by extraction with a 1 M aqueous solution of NaOH, followed by drying with $MgSO_4$, and distilled. Benzoyl peroxide was recrystallized from a mixture of chloroform and methanol. 2-Fluorobiphenyl-2′-carboxylic acid (**6**) was prepared according to a literature method.[15] All reference compounds were available from earlier work.[10]

General Procedure, Electrolysis. The electrolysis was carried out at the appropriate temperature in a 20-mL undivided cell equipped with two platinum foil electrodes (2 cm^2 each). The calculated amount of charge was passed through the solution (10 mL, 0.5 M in substrate) at a constant current (5 mA/cm^2) using an Amel 552 potentiostat. The reaction mixture was worked up by addition of water (50 mL) and extraction twice with CH_2Cl_2. The organic phase was washed with a saturated aqueous $NaHCO_3$ solution, dried, and evaporated.

Benzoyl Peroxide Initiation. This was carried out as described earlier.[7]

Preparation of 1-Fluoro-4-acetoxynaphthalene (1c). A 0.5 M solution of KOAc in glacial acetic acid (75 mL) containing 0.04 mol of 1 was electrolyzed at 20 °C, by using a platinum anode (30 cm^2) and a platinum cathode (5 cm^2) at a constant current of 300 mA. After passage of 2 F/mol, the reaction mixture was poured onto water (150 mL). The solution was extracted twice with CH_2Cl_2, and the organic phase washed with a saturated aqueous solution of $NaHCO_3$, dried, and evaporated. GLC analysis indicated the presence of 1 and 1c in a ratio of 56:44. The reaction mixture was distilled on a kugelrohr apparatus (bath temperature 80 °C (0.1 mmHg)) giving 1.61 g of a mixture of 1 and 1c. Pure 1c (0.3 g, 10 %) was isolated after flash chromatography on a silica gel column with a pentane–chloroform mixture (4:1, v/v) as eluent. The product could be recrystallized from cyclohexane, mp 68–69 °C;[16] mass spectrum, *m/e* (relative intensity) 204 (M^+, 7), 162 (100), 134 (25), 133 (55); ^1H NMR ($CDCl_3$) δ 2.44 (3 H, s), 7.11 and 7.16 (2 H, AB quartet doubled by ^{19}F–^1H coupling, $J_{AB} = 8.4$ Hz, J (^{19}F–H_2) = 9.6 Hz, J (^{19}F–H_3) = 4.7 Hz), 7.53–7.59 (2 H, m), 7.80–7.86 (1 H, m), 8.07–8.13 (1 H, m).

Oxidations with Peroxydisulfate and Copper(III). A mixture of the aromatic compound (2 mmol), oxidant (0.5 mmol), and glacial acetic acid/0.5 M KOAc (10 mL) was stirred at reflux temperature. The reaction period was 2 h, copper(II) was added as copper(II) acetate. The workup procedure and analysis were

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(12) The effect observed on addition of $Cu(OAc)_2$ to these reactions is not drastic but nevertheless significant; on initiation with BPO the ratio of **1a** to **1b**, equivalent to the number of cycles initiated by the benzoyloxy radical is lowered from 24 to 8 and on oxidation of **1** with Cu(III) the yield of **1a** is decreased by a factor of 2.9.

(13) Giordano, C.; Belli, A.; Citterio, A.; Minisci, F. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1574.

(14) Neta, P.; Madhavan, V.; Zemel, H.; Fessenden, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 163.

(15) Gilman, H.; Gorsich, R. D. *J. Am. Chem. Soc.* **1956**, *78*, 2217.

(16) A satisfactory elemental analysis (C, H) was obtained for this compound.

carried out as described earlier.[6]

Acknowledgment. We gratefully acknowledge valuable discussions with Prof. L. Eberson. We thank Kristina Stenvall for the skillful preparation of 2-fluorobiphenyl-2′-carboxylic acid. This work was supported by grants from the Swedish Natural Science Research Council.

Registry No. **1**, 321-38-0; **1c**, 90990-92-4; **2**, 323-09-1; **3**, 459-60-9; **4**, 321-28-8; **6**, 361-92-2.

Reactivities of Acylperoxy Radicals in the Photoreaction of α-Diketones and Oxygen

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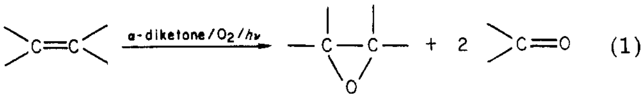
Received March 1, 1984

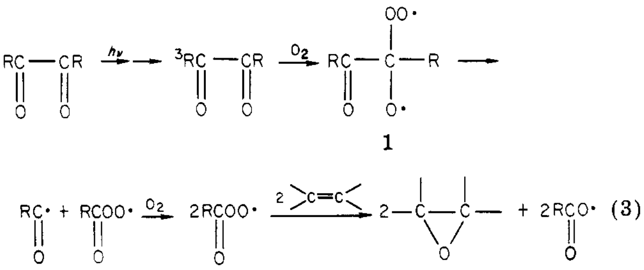
The photoepoxidation of olefins with α-diketones and oxygen has been studied mechanistically focusing on the reactivities of intermediate radicals. One mole of α-diketone resulted in the formation of 2 mol of epoxide together with 2 equiv of C–C cleavage of olefins. The photoepoxidation proceeds via acylperoxy radicals $RCO_3\cdot$ and the C–C cleavage of olefins is caused by acyloxy radical $RCO_2\cdot$. The addition of $RCO_3\cdot$ to olefins was found to be ca. 10^5-fold faster than that of alkylperoxy radical ROO·. The relative reactivities of olefins suggest that acylperoxy radicals behave as a strongly electrophilic radical. That is, ρ values of -1 (vs. σ^+) obtained in the photoepoxidation of substituted styrenes are of the same magnitude as those in the epoxidation with molecular peracids. Although the relative reactivities of olefins toward the photoepoxidation roughly parallel those for the peracid epoxidations, the additivity of methyl substituent is not always operative. This is explained by a steric retardation by too many substituents on the carbon attacked by $RCO_3\cdot$ in addition to the relative stabilities of resulting adduct radicals between olefins and $RCO_3\cdot$. Since acylperoxy radicals are not reactive toward sulfides, sulfoxides, or pyridine, a selective epoxidation of double bonds is possible. The relative reactivities of olefins toward benzoyloxy and methylperoxy radicals revealed a much less electrophilic nature of these oxy radicals, the ρ values for styrenes being -0.1 to -0.2.

α-Diketone-sensitized photoepoxidation (eq 1) as reported by Bartlett et al.[1,2] is interesting in relation to a Schenck mechanism (eq 2)[3] in sensitized photooxidations.



$$\text{Sens} \xrightarrow{h\nu} {}^1\text{Sens} \longrightarrow {}^3\text{Sens} \xrightarrow{O_2} \dot{\text{Sens}}\text{-OO}\cdot \longrightarrow \text{Oxygenation} \qquad (2)$$

Recently we have suggested that the photoepoxidation proceeds via acylperoxy radicals $RCO_3\cdot$ generated by the photooxidation of α-diketones under oxygen.[4] That is, a reaction sequence as outlined in eq 3 is proposed from the facts that benzil is not a recycling sensitizer but photooxidized to benzoic or peroxybenzoic acid and phenyl benzoate in benzene, just as reported by Saltiel,[5] and that its photooxidation rate is not affected by the addition of olefins.



In order to ascertain whether acylperoxy radicals are the inermediary O-transfer species and to examine their reactivities, we planned to study the stoichiometry of the reaction together with relative reactivities for olefins and other substrates. Herein, we report that the photoepoxidation proceeds via acylperoxy radicals which behave as a strongly electrophilic radical toward olefins. The results are similar with those of the photoepoxidation with benzoin and oxygen,[6] suggesting the same O-transfer reagent.

Results and Discussion

The photolysis of benzil is very slow under nitrogen but proceeds smoothly under oxygen.[4,5] The photooxidation rate was not changed by the addition of olefins and the resulting stoichiometry of epoxide:α-diketone consumed was mostly in the range of 1–2 but sometimes increased up to 3.[1a,4] The latter high ratio of 3 and the accompanying C–C cleavage of olefins could not be explained by the proposed pathway (eq 3).

Epoxidation vs. C–C Cleavage. The photoepoxidation with α-diketone and oxygen accompanies the C–C cleavage of olefins.[1,4] Interestingly, the epoxidation and C–C cleavage is found to be dependent on the olefin concentrations. For example, the following results were obtained

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(1) (a) Shimizu, N.; Bartlett, P. D. *J. Am. Chem. Soc.* **1976**, *98*, 4193. (b) Bartlett, P. D.; Becherer, J. *Tetrahedron Lett.* **1978**, 2983.

(2) Recently, it has been stated that benzil is not always a sensitizer. (a) Bartlett, P. D.; Roof, A. A. M.; Shimizu, N. *J. Am. Chem. Soc.* **1982**, *104*, 3130. (b) Clennan, E. L.; Speth, D, R.; Bartlett, P. D. *J. Org. Chem.* **1983**, *48*, 1246.

(3) For example, (a) Schenck, G. O. *Angew. Chem.* **1957**, *69*, 579. (b) Gollnick, K. *Adv. Photochem.* **1968**, *6*, 1.

(4) Sawaki, Y.; Foote, C. S. *J. Org. Chem.* **1983**, *48*, 4934.

(5) Saltiel, J.; Curtis, H. C. *Mol. Photochem.* **1969**, *1*, 239.

(6) Sawaki, Y.; Ogata, Y. *J. Am. Chem. Soc.* **1981**, *103*, 2049.