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ONE ELECTRON OXIDATIONS OF BENZYL AND 2-PHENYLETHYL PHENYL ETHERS. THE FATE OF THE INTERMEDIATE RADICAL CATIONS

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Abstract - The one electron oxidations of benzyl phenyl ether (1), 2-phenylethyl phenyl ether (2) and 2-(4-methoxyphenyl)ethyl phenyl ether (3) promoted (a) by cerium(IV) ammonium nitrate (CAN) in AcOH, (b) electrochemically in AcOH-MeCN/AcOK and (c) photochemically in MeCN, in the presence of 9,10-dicyanoanthracene (DCA), have been investigated. With 1 benzaldehyde forms, under all the reaction conditions, accompanied by products of acetoxylation at the phenoxy ring (conditions a and b) or by phenyl benzoate (condition c). The CAN-promoted and the electrochemical oxidation of 2 exclusively lead to substitution at the phenoxy ring, whereas only side-chain attack at the benzylic carbon occurs in all of the reactions of 3, with formation of 4-methoxybenzaldehyde and products of side-chain oxidation. Phenyl 4-methoxybenzoate is also formed (conditions b and c). However, when the electrochemical oxidation is carried out in the absence of AcOK, only a product of intramolecular ring closure forms. These results allow one to draw some interesting conclusion on the competition between the various reaction pathways available to the cation radicals which are the first formed reaction intermediates in these one electron processes.

Aromatic radical cations present a very rich chemistry as they react with nucleophiles according to a variety of reaction pathways. Nuclear and side-chain reactions are possible and in the latters there is further competition between processes involving C-H bond breaking and those where C-C and (or) C-X (X=heteroatom) bond cleavage occurs. An additional possibility is the attack of the nucleophile at the heteroatom (i.e. when X=S) to give heteroatom-functionalized products.

In the last few years it have become apparent that aromatic radical cations can play a very important role in a great number of organic reactions.[1] There is therefore a continuous interest for studies concerning the reactions of these species and the structural factors which influence their relative importance.

The one electron oxidations of benzyl and 2-phenylethyl ethers provide us with significant information in this respect since the intermediate radical cations can undergo side-chain C-H, C-C and C-O bond breaking, in addition to reactions at the aromatic ring. Accordingly, the reactions of these ethers have been intensively investigated in the past.[2-7]

According to these studies, proton loss is the most favoured pathway[2,3,4,6,7] of dibenzyl and alkyl benzyl ethers radical cations, even though the possibility of C-O bond cleavage has been suggested.[5] In contrast, with 2-phenylethyl alkyl ethers radical cations, the major processes are reported to be the cleavage of C-O and C-C bonds.[3]

With the aim of getting further information on this problem and of comparing the behaviors of phenyl ethers with those of their alkyl counterparts, we have investigated some one electron oxidation reactions of benzyl phenyl ether (1), 2-phenylethyl phenyl ether (2) and 2-(4-methoxyphenyl)ethyl phenyl ether (3). In the reactions of 1 and 2 electron loss should concern the phenoxy ring and radical cations with an electronic structure different from that of the previously studied systems should be obtained.

The one electron oxidation reactions have been promoted by ceric ammonium nitrate (CAN), electrochemically, and photochemically, by dioxygen in the presence of 9,10-dicyanoanthracene (DCA). There is clear evidence that all these oxidizing systems involve the formation of a radical cation intermediate.[8]

It has to be added that benzyl and 2-phenylethyl phenyl ethers are coal model compounds;[12] thus, the study of one electron oxidations of these ethers may also give useful information with respect to the possible use of one electron transfer processes to convert coal in more mobile compounds under mild conditions. Moreover, formation of benzyl ethers is frequently used to protect the alcoholic group: reactions leading to the cleavage of these compounds are therefore of synthetic interest.

RESULTS

The distribution of products in the oxidations of compounds 1-3 is reported in the Table, where are also stated the reaction conditions. The yields refer to isolated material which has been identified, in most cases, by comparison with authentic specimens. These yields have been found in good agreement with those determined by NMR analysis of the crude reaction product and the material balance has generally been satisfactory (in most cases more than 90%). An 1:1 substrate:CAN molar ratio has been used, that is twice the stoichiometric one in order to reduce the possibility of overoxidation of the reaction products.

Benzyl phenyl ether (1). With CAN in AcOH at 50°C the reaction leads to a cleavage product (benzaldehyde) and to products of nuclear substitution, acetoxy and nitro derivatives, involving the attack at the oxygen bearing aromatic ring. The nitro derivatives are certainly formed in a side-process, since it is well known that CAN can also behave as a nitrating agent.[13] Their formation has no relation with the problem under investigation and will not be commented further.

In the anodic oxidation in AcOH-MeCN, in the presence of AcOK, ring acetoxylation is the predominant reaction. Other products are benzaldehyde and α-acetoxybenzyl phenyl ether (4). No reaction takes place when the electrochemical oxidation is carried out in the presence of Et_4NBF_4, most of the starting material being recovered.

Benzaldehyde is also formed in the DCA-photosensitized oxidation of 1 together with comparable amounts of phenyl benzoate.

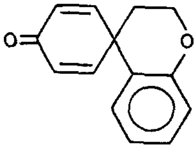
It should be noted that in the cleavage reactions, beside benzaldehyde, also phenol should form. Phenol, however is very reactive with the oxidant systems used leading to a very complex mixture of products. No attempt was carried out to identify these products.

2-Phenylethyl phenyl ether (2). With CAN in AcOH the only reaction is that leading to the products of acetoxylation at the phenoxy ring. Also in this case there is, as observed with 1, nuclear nitration, which is in fact the major process.

Ring acetoxylation is the exclusive reaction observed in the anodic oxidation of 2, in the presence of AcOK, whereas no reaction takes place when 2 is irradiated in MeCN, in the presence of DCA.

2-(4-Methoxyphenyl)ethyl phenyl ether (3). In the reaction with CAN the cleavage product, 4-methoxybenzaldehyde, and the side-chain substitution products, 4-methoxy-α-phenoxyacetophenone (5) and 2-acetoxy-2-(4-methoxyphenyl)ethyl phenyl ether (6), are formed. The same three products also form in the anodic oxidation in the presence of AcOK.

Interestingly, a different outcome is observed when the electrochemical reaction is carried out in the presence of Et_4NBF_4: only product 7 forms.



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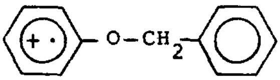
4-Methoxybenzaldehyde and 5 are the products obtained in the DCA photosensitized oxidation.

There was no attempt to identify the phenolic products which, together with formaldehyde, should accompany the formation of 4-methoxy-benzaldehyde in the cleavage reactions.

DISCUSSION

The results for the ether 1 can conveniently be discussed on the basis of the very reasonable assumption that in all oxidizing systems the electron is exclusively lost from the phenoxy ring to give the radical cation 8. This hypothesis is fully justified by the great difference between the oxidation potentials of anisole (2.2 V vs. NHE) and toluene (2.7 V).[14]

Nuclear attack by AcO^- and AcOH at the positively charged ring of 8 accounts for the observed formation of acetoxylated products in the electrochemical and CAN-promoted oxidations, respectively. The proportion of ring attack, with respect to side-chain attack (see infra), is significantly larger in the anodic oxidation than in the



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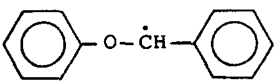

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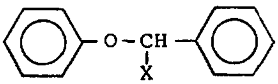

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CAN-promoted reaction. The favorable effect of AcOK in promoting nuclear reaction in anodic oxidations has been already observed.[15]

No nuclear reaction is observed in the photochemical process in MeCN, in agreement with the very low capability of this solvent to attack the ring carbons of aromatic radical cations.[16]

A cleavage product, benzaldehyde, is also present in the CAN-promoted reaction of 1. However, it is highly unlikely that C-O bond rupture has occurred to the state of 8, as in this case the benzyl radical would have formed, leading to benzyl acetate and/or nitrate, which have not been observed.

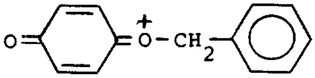
A more plausible hypothesis is that first 8 undergoes proton loss from the methylene group to give the α-phenoxybenzyl radical 9. Oxidation of 9 by CAN should lead to 10 (X=OAc, ONO_2), as already shown for other benzyl radicals.[10b] 10 can easily be converted to benzaldehyde under the acid reaction conditions.

Clear evidence for the possible formation of 10 (X=OAc) is found in the anodic oxidation of 1 in the presence of AcOK, where indeed 10 (X=OAc) is one of the reaction products. It certainly derives from the anodic oxidation of 9 to a carbocation which can then react with the solvent AcOH. Probably, in the electrochemical reaction, the presence of the strong base AcOK slows down the hydrolysis rate of 10 to benzaldehyde.

Interestingly, no significant reaction takes place when the anodic oxidation of 1 is carried out in the presence of Et_4NBF_4. Thus AcOK seems necessary, not only for the nuclear reaction,[15] but for the deprotonation of 8. Presumably, on the absence of a strong base 8 reverts back to the starting material.

The formation of benzaldehyde in the photochemical autoxidation of 1 can be accounted for as above. The α-phenoxy radical 9 should still be the critical intermediate, which may react with dioxygen to give the hemiacetal 10 (X=OH), in several steps. The latter can be converted to benzaldehyde by acid hydrolysis or, it can be further oxidized to form phenyl benzoate, the other product of the photochemical reaction. Formation of esters has frequently been observed in several oxidations of benzyl ethers, including the TiO_2-sensitized photooxidation.[2]

Proton loss from 8 is noteworthy since the hydrogen bearing carbon is bonded to the uncharged ring. Probably, as shown in the resonance structure 11, part of the positive charge of 8 is delocalized on the oxygen atom, which should enhance the acid character of the adjacent C-H bonds. This is also supported by ESR studies of methoxybenzene radical cations, which indicate significative hyperfine coupling constants of the OCH_3 protons.[17]



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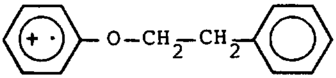
The benzylic nature of CH_2 protons should also play a role in this respect since both in the CAN-induced and electrochemical oxidation of 2-phenylethyl phenyl ether (2), the only products observed are those of nuclear acetoxylation. Clearly, no proton loss occurs from the radical cation 12 where the CH_2 protons adjacent to oxygen are not enzylic.



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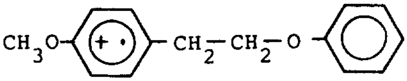
The study of the reactions of 2-(4-methoxyphenyl)ethyl phenyl ether 3 provides information on the behaviors of a cation radical, like 13, where, differently than with 8 and 12, the positive charge should be now located on the 4-methoxybenzyl ring (effect of a methoxy and a para-alkyl group).



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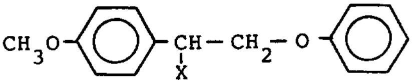

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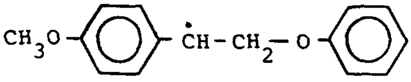
Accordingly, the benzylic acetoxy derivative 14 (X=OAc) is the only product observed in the anodic oxidation of 3 in the presence of AcOK and the major product in the CAN-promoted oxidation of 3 in AcOH. In both cases 14 (X=OAc) should derive from the benzyl radical 15, formed by deprotonation of 13.



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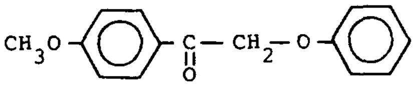

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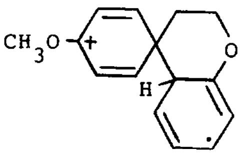
In the CAN-promoted reaction further oxidation of 14(X=OAc) leads to the ketone 16 and to a product of C-C bond cleavage, p-methoxybenzaldehyde. C-C bond cleavage to the state of 13 can, however, be excluded since neither 4-methoxybenzyl acetate nor 4-methoxybenzyl nitrate are among the reaction products.

A similar situation should hold in the DCA-sensitized photochemical autoxidation of 3. The benzyl radical 15 can react with O_2 to eventually give 14 (X=OH), which is converted to 4-methoxybenzaldehyde by hydrolysis, and to the ketone 16, by oxidation.

Interestingly, a completely different result is obtained in the anodic oxidation of 3 in the presence of Et_4NBF_4, where the only observed product has been the spirodienone 7. Probably, in the absence of AcOK, deprotonation from 13 is made more difficult and an intramolecular reaction involving the phenoxy and the positively charged ring takes place. This reaction should lead to 17, which might than



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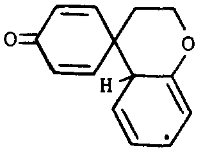

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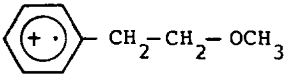
undergo demethylation to 18. The latter should easily produce 7 by oxidation and proton loss.

The observation that under all our reaction conditions 13 does not undergo C-C bond cleavage, to give a benzyl radical and a very stable α-phenoxycarbocation, is remarcable since it contrasts with results concerning the oxidation of 2-phenylethyl methyl ether (19) by $SO_4^{\cdot -}$,[3] where evidence for this type of cleavage and also for C-O bond cleavage has been obtained.

To test if this difference is due to 2 being a phenyl ether whereas 19 is an alkyl ether, we have also carried out some anodic and CAN-promoted oxidations of the latter substrate. However, even with 19 no evidence for the formation of benzyl acetate has been found. This confirms that also for the radical cation 20 C-C bond cleavage is not a suitable pathway, under our reaction conditions.



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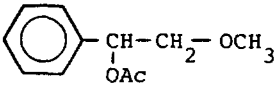

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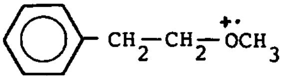
The acetoxy derivative 21 is the exclusive product in the CAN-promoted reaction of 19 and the main product in the anodic oxidation of the same substrate, where it is accompanied by small amounts of benzaldehyde. Certainly, proton loss is the most favoured reaction of 20, which, as usual, leads to a benzyl radical from which 21 can be formed. Some oxidation of 21 to benzaldehyde may also take place, as observed in the electrochemical reaction.

Tentatively, the different behavior of $SO_4^{\cdot -}$ with respect to our oxidizing systems in the oxidation of 2-phenylethyl ethers might be related to the quite high temperature (100°C) required by the former oxidant. This might induce the occurrence of processes (namely C-C and C-O bond breaking) which have no chance to compete with C-H bond rupture at the lower temperature (50°C or less) used in this work.

Another hypothesis is that $SO_4^{\cdot -}$ ($E°= 2.5-3.0$ V vs. NHE)[18] is a much stronger oxidant than CAN ($E°=1.3$ V)[19] and the excited state of DCA ($E°=2.0$ V).[11] Thus, $SO_4^{\cdot -}$ might also abstract an electron from the oxygen atom of 19 to give the cation radical 22. As suggested by Walling and coworkers, 22 might undergo C-C and C-O bond cleavage to



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give the products (benzyl and 2-phenylethyl acetate) formed in the $SO_4^{-\cdot}$ induced oxidation of 19.

Whatever the explanation, it seem clear from our results, that the most preferred pathway for both benzyl and 2-phenylethyl ethers radical cations is the loss of a benzylic proton. Apparently, breaking of C-C and C-O bonds can also occur, but under quite drastic conditions and when very strong oxidants are used.

Probably, to observe C-C bond cleavage under mild conditions, the radical cation should form carbon radicals more stable than benzyl radicals. Accordingly, this type of cleavage occurs to a large extent in the photosensitized oxidations of 2,2-diphenylmethyl ethers,[20] where the intermediate radical cations cleave to give diphenylmethyl radical along with the α-alkoxy carbocations.

EXPERIMENTAL

^1H NMR spectra were obtained from a Bruker WP 80 CW (at 80 MHz) and Varian EM 390 (at 90 MHz) spectrometers, for solutions in $CDCl_3$. GCMS analyses were performed on a Hewlett Packard gaschromatograph 5890A (SE30 capillary column, 12m, at 70 to 300°C) connected with a mass selective detector 5970 (at 70 eV). Elemental analyses were carried out on a Carlo Erba Elemental Analyzer M1106. All melting points were uncorrected.

Starting Materials. Ceric Ammonium Nitrate, $(NH_4)_2Ce(NO_3)_6$, dried at 85°C for 1h before use, was a commercial sample. 9,10-Dicyanoantracene (DCA) was prepared as previously described.[21] Benzyl phenyl ether (1), 2-phenylethyl phenyl ether (2), and 2-(4-methoxy-phenyl)ethyl phenyl ether (3) were obtained by the reaction of benzyl, 2-phenylethyl and 2-(4-methoxyphenyl)ethyl bromide, respectively, and phenol in refluxing aceton in the presence of an equimolar amount of sodium carbonate. 1: 49%, mp=38°C (lit.[22] mp 38.4°C); 2: 47%, NMR δ 7.3-6.7 (m,10H,ArH), 4.10 (t,J=6.5Hz,2H,CH_2-O), 3.07 (t,J=6.5Hz,2H, Ph-CH_2); 3: 33%, NMR δ 7.3-6.7 (m,9H,ArH), 4.08 (t,J=6.5Hz,2H,CH_3-O), 3.70 (s,3H,CH_3), 2.98 (t,J=6.5Hz,2H,Ar-CH_2). 2-Phenylethyl methyl ether (19) was obtained by methylation of sodium 2-phenylethoxide with CH_3I in anhydrous DMSO: 63%, NMR δ 7.25 (s,5H,ArH), 3.61 (t,J=6.5Hz, 2H,CH_2-O), 2.90 (t,J=6.5Hz,2H,Ph-CH_2).

Reactions with CAN. The substrate (10 mmol) was added to a suspension of CAN (10 mmol) in acetic acid (150 mL). The mixture was allowed to react at 40 or 50°C, according to substrate reactivity (see table), until a pale yellow solution and a white precipitate were observed. The mixture was poured into cold water and extracted with ether. The combined organic extracts were washed with water, dried and concentrated. The residue was cromatographed eluting with light petroleum-diethyl ether (4:1).

From 1 the products were benzaldehyde (comparison with a commercial sample), benzyl 4-nitrophenyl ether (23) [comparison with an authentic specimen obtained by the reaction of benzyl bromide with 4-nitrophenoxyde in DMF: NMR δ 8.3-7.0 (four peaks,AA'XX'system,4H,ArH) 7.40 (s,5H,ArH), 5.15 (s,2H,CH_2); MS m/z (rel.intensity) 229 M^+, 91 (100)], a mixture of isomeric monoacetoxyphenyl benzyl ethers [NMR δ 7.5-6.8 (m,9H,ArH), 5.07 (s,2H,CH_2), 2.28 (s,3H,CH_3); MS of two GC peaks, m/z (rel.intensity) 242 M^+,200,109,91(100),65; Anal.Calcd for $C_{15}H_{14}O_3$: C,74.36; H,5.82. Found: C,74.30; H,5.84], and benzy 2-nitrophenyl ether [comparison with an authentic specimen prepared, as 23, starting from 2-nitrophenoxide: NMR δ 7.9-6.9 (m,9H,ArH), 5.19 (s,2H,CH_2); MS m/z (rel.intensity) 229 M^+, 91(100)].

The reaction products from 2 were: 4-nitrophenyl 2-phenylethyl ether [comparison with an authentic specimen obtained by the reaction of 2-phenylethyl bromide with 4-nitrophenoxide in DMF: NMR δ 8.2-6.8 (four peaks,AA'XX' system,4H,ArH), 7.30 (s,5H,ArH), 4.30 (t,J=6.5Hz, 2H,CH_2O), 3.11 (t,J=6.5Hz,2H,CH_2); MS m/z (rel.intensity) 243 M^+, 105(100),77], a mixture of isomeric monoacetoxyphenyl 2-phenylethyl ethers [NMR δ 7.4-6.8 (m,9H,ArH), 4.20 (t,J=6.5Hz,2H,CH_2O), 3.02 (t,J=6.5Hz,2H,CH_2), 2.17 (s,3H,CH_3); MS of three GC peacks, m/z (rel. intensity) 256 M^+,214,105(100),77; Anal.Calcd for $C_{16}H_{16}O_3$: C,74.98; H,6.29. Found: C,74.90; H,6.25], and 2-nitrophenyl 2-phenylethyl ether [comparison with an authentic specimen prepared as 6 starting from 2-nitrophenoxide: NMR δ 7.9-6.9 (m,9H,ArH), 4.30(t,J=6.5Hz,2H,OCH_2), 3.12 (t,J=6.5Hz,2H,CH_2); MS m/z (rel.intensity) 243 M^+,105(100),77].

Reaction of 3 gave 4-methoxybenzaldehyde (comparison with a commercial sample, 4-methoxy-α-phenoxyacetophenone (5) [NMR δ 7.9-8.1 (two peaks, AA′ portion of an AA′XX′ system,2H,ArH), 7.1-6.9 (m,7H,ArH), 5.18 (s,2H,CH_2), 3.80 (s,3H,CH_3); MS m/z (rel.intensity) 242 M^+, 135(100),107,92,77; Anal.Calcd for $C_{15}H_{14}O_3$: C,74.36; H,5.82. Found: C,74.41; H,5.85] and 2-acetoxy-2-(4-methoxyphenyl)ethyl phenyl ether (6)[NMR δ 7.4-6.8 (m,9H,ArH), 6.2-6.0 (four peaks, X portion of an ABX system,1H,CH), 4.4-4.0 (eight peaks, AB portion of an ABX system, 2H,CH_2), 3.78 (s,3H,OCH_3), 2.10 (s,3H,$COCH_3$); MS m/z (rel.intensity) 286 M^+,226(100),193,165,137,91,77; Anal.Calcd for $C_{17}H_{18}O_4$: C,71.31; H,6.33. Found: C,71.20; H,6.39].

19 yielded 2-acetoxy-2-phenylethyl methyl ether (21): NMR δ 7.3 (s,5H,ArH), 6.0-5.8 (m, X portion of an ABX system,1H,CH), 4.7-4.3 (m, AB portion of an ABX system,2H,CH_2), 3.29 (s,3H,OCH_3) 2.00 (s,3H, $OCOCH_3$); MS m/z (rel.intensity) 162 (M^+-CH_3OH), 149,134,107(100), 91,43.

Anodic Oxidations. The electrochemical experiments were performed in a jacketed microcell thermostated at 25°C with Pt as anode (4 cm^2 effective electrode area) and cathode. The magnetically stirred solutions were electrolyzed by using an AMEL 552 potentiostat until 1F mol^{-1} of charge were passed. The ether (4.4 mmol) was dissolved in an acetic acid acetonitrile (3:1, v/v) mixture (50 mL) containing AcOK 0.1M or Et_4NBF_4 0.07M. The solution was electrolyzed at 1.8V (*vs.* SCE) constant potential and 20-30 mA cm^{-1}. The reaction mixture was worked up as above.

(A) *Electrolysis in the presence of AcOK*. Anodic oxidation of 1 gave benzaldehyde, a mixture of isomeric benzyl monoacethoxyphenyl ethers (see reaction with CAN) and α-acetoxybenzyl phenyl ether (4) [NMR δ 7.7-6.9 (m,11H,ArH and CH), 2.05 (s,3H,CH_3); MS m/z (rel. intensity) 242 M^+,182,136,94(100),77,43].

From 2 a mixture of isomeric monoacethoxyphenyl-2-phenylethyl ethers (see reaction with CAN) was obtained.

The products of the anodic oxidation of 3 were 5,6 and 4-methoxybenzaldehyde.

(B) Electrolysis in the presence of Et_4NBF_4. No reaction products were observed from 1 and 2 while 3 yielded the spyrodienone (7) as the only product [NMR δ 7.3-6.8 (m,6H,ArH and CH), 6.30 (d,J=10Hz,2H,CH), 4.30 (m,2H,CH_2), 2.10 (m,2H,CH_2); MS m/z (rel.intensity) 212 M^+(100), 184,169,128, 102,77; Anal.Calcd for $C_{14}H_{12}O_2$: C,79.22; H,5.70. Found: C,79.10; H,5.67]. No product was observed when the reaction was performed in pure CH_3CN.From 19 it was obtained 21 and benzaldehyde as above.

Photochemical Autoxydation. A dioxygen bubbled solution of the ether (4 mmol) and DCA (0.02 mmol) in CH_3CN (100 mL) was irradiated with an external high-pressure mercury lamp (Helios-Italquartz, 500W, pyrex filter) at room temperature for 1.5h and the mixture was worked up as previously described.

From 1 it was obtained benzaldehyde and phenyl benzoate (comparison with a commercial sample); no reaction product was detected from 2; 3 yielded 4-methoxybenzaldehyde and 5.

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8. The occurrence of an ECE mechanism for the anodic oxidations of alkylaromatics is well demonstrated[9] and there is no doubt that it should also operate with the substrates investigated here. The operation of an electron transfer mechanism for CAN-promoted oxidations of alkylbenzenes has also been shown by previous work of our group.[10].

Finally, the excited state of DCA is a strong oxidant certainly capable to generate alkylaromatic radical cations.[11]

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16. As far as we known is no example has been reported of photo-induced ring acetamidation of aromatic systems. Probably, once the DCA$^{-\bullet}$ ArH$^{+\bullet}$ pair is formed, back electron transfer is much faster than the reaction of ArH$^{+\bullet}$ with MeCN.

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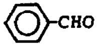
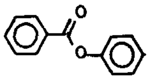
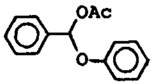
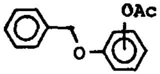
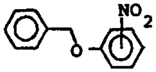
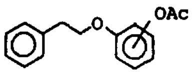
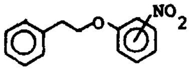
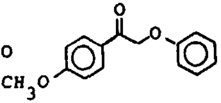
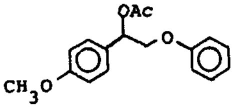
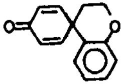
Table - Products Yields in Some Oxidations of Benzyl Phenyl Ether (1), Phenethyl Phenyl Ether (2) and 4-Methoxyphenethyl Phenyl Ether (3).

Reaction conditions	Substrate, %[a]	Products, %[a]				
Reactions of 1						
CAN[b], AcOH, 50°C	75	11			6	4
A.O., AcOH-CH_3CN, AcOK[c]	74	2		2	13	
A.O., AcOH-CH_3CN, Et_4NBF_4[d]	90			no reaction		
DCA, hν, O_2, CH_3CN[f]	86	8	6			
Reactions of 2						
CAN[b], AcOH, 50°C	69	6			16	
A.O., AcOH-CH_3CN, AcOK[c]	75	12				
A.O., AcOH-CH_3CN, Et_4NBF_4[d]	92			no reaction		
DCA, hν, O_2, CH_3CN[f]	90			no reaction		
Reactions of 3						
CAN[b], AcOH, 40°C	74	3	4		9	
A.O., AcOH-CH_3CN, AcOK[c]	56	6	5		16	
A.O., AcOH-CH_3CN, Et_4NBF_4[d,g]	55					26
DCA, hν, O_2, CH_3CN[f]	80	8	3			

[a] % of recovered material with respect to the starting substrate (4 mmol). The error is ±2. [b] [CAN] = 0.07M. [c] Anodic oxidation, in acetic acid:acetonitrile (3:1) with AcOK, 0.1M. Controlled potential, 1F mol^{-1} at 1.8V vs. SCE. [d] See note c, in the presence of Et_4NBF_4, 0.07M. [e] [CAN] = 0.08M. [f] [DCA] = $2x10^{-4}$M. [g] No products were observed in CH_3CN.