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# ELECTROOXIDATIVE FRAGMENTATION OF BENZYLIC ALDEHYDES AND KETONES

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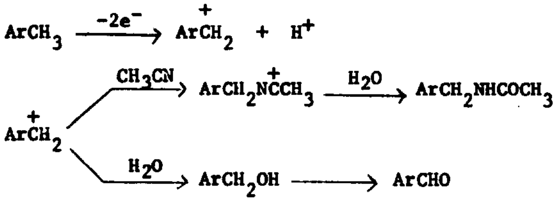
The electrooxidation of alkyl aromatics has attracted considerable attention.[1-6] In acetonitrile solvent side chain substituted acetamides as well as alcohols and carbonyl products (from adventitious water) are obtained. Although an accurate mechanistic evaluation of the early steps of this reaction has not been made, the process can be adequately represented as follows:



We have found the electrooxidation of compounds of the type 1 leads to carbon-carbon bond cleavage apparently involving intermediate benzylic cations and acylium ions. This reaction is of

$$\underset{R}{\mathrm{PhCH}}\mathrm{-COR'}$$

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special interest because it mimics the mass spectral fragmentation of these compounds.

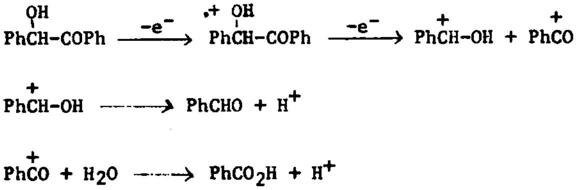
The oxidations were performed potentiostatically in a three compartment cell. The anode was platinum sheet (total area 2 in$^2$), the reference electrode Ag/AgNO$_3$ in acetonitrile and the electrolyte mixture, acetonitrile-lithium perchlorate. Sodium carbonate was included to scavenge acid and preclude acid catalyzed reactions. Initial currents ranged from 150-500 ma depending on the compound. In order to sustain high currents, the potential was pulsed to more negative values (~0 v) for one second every ten seconds. Electrolysis was discontinued when the current dropped to 5-10 ma and the products (Table I) were identified spectroscopically and by comparison with authentic samples. The pulsing technique has proven invaluable to avoid electrode passivation. The oxidation of benzylic alcohols is reported to be impossible because very little current is passed. We find that regularly pulsing the voltage to values near zero volts carries out very little reduction but does clean the electrode surface allowing aldehyde and ketone formation.

TABLE I. Electrooxidation Products in Acetonitrile.

| Reactant (mmoles) | millifaradays | V[a.] | Products (mmoles) |
|---|---|---|---|
| $Ph_2CH$-COPh (1.8) | 8.2 | 1.82 | $Ph_2CO$ (1.1), $PhCO_2H$ (1.1) |
| $Ph_2CH$-CHO (5.1) | 14.7 | 1.71 | $Ph_2CO$ (2.7), $Ph_2CHNHCOCH_3$ (0.5) |
| $PhCH_2$-COPh (5.1) | 23 | 1.85 | $PhCO_2H$ (2.5), PhCOCOPh (1.6), PhCHO (0.3) |
| Ph-$CH(CH_3)CHO$ (5.6) | 16 | 1.80 | $PhCH(CH_3)NHCOCH_3$ (0.6), $PhCOCH_3$ (0.4) |
| PhCH(OH)COPh (2.0) | 4.4 | 1.89 | PhCHO (0.7), $PhCO_2H$ (1.5), PhCOCOPh (0.7) |
| PhCH(OH)COPh (2.0)[b.] | 4.4 | 1.90 | PhCHO (1.4), $PhCO_2H$ (1.5) |
| $Ph_2CHOH$ (5.4) | 7.3 | 1.70 | $Ph_2CO$ (3.4), $Ph_2CHOCHPh_2$ (1.2) |

a. Reference electrode - Ag/0.1N$AgNO_3$ in acetonitrile. b. Under argon.

It is clear that cleavage of the benzylic carbon-carbonyl carbon bond is quite favorable and can compete with side chain acetamidation. This seems characteristic of cleavage of an acyl fragment. Under the above conditions ethyl benzene produces acetophenone and N-(1-phenylethyl)-acetamide, not benzoic acid or benzaldehyde. From a mechanistic viewpoint, benzoin oxidation is particularly uncomplicated and must proceed approximately as follows:



$$\mathrm{Ph}\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{H\text{-}COPh} \xrightarrow{-e^-} \overset{\cdot+}{\mathrm{Ph}}\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{H\text{-}COPh} \xrightarrow{-e^-} \mathrm{Ph}\overset{+}{\mathrm{C}}\mathrm{H\text{-}OH} + \mathrm{Ph}\overset{+}{\mathrm{C}}\mathrm{O}$$

$$\mathrm{Ph}\overset{+}{\mathrm{C}}\mathrm{H\text{-}OH} \longrightarrow \mathrm{PhCHO} + \mathrm{H}^+$$

$$\mathrm{Ph}\overset{+}{\mathrm{C}}\mathrm{O} + \mathrm{H_2O} \longrightarrow \mathrm{PhCO_2H} + \mathrm{H}^+$$

Since neither aliphatic acyloins nor benzoyl type compónds, *e.g.*, benzaldehyde, benzophenone, benzoic acid, are oxidized at this potential initial electron transfer must be from the benzylic phenyl group. Loss of a $\pi$ electron from a benzylic moiety should, indeed, take place at about 1.8 v.[7] The initially formed cation radical will be very unstable so that cleavage and a second electron transfer will rapidly follow.[8] Scavenging of benzoyl cations by adventitious water[9] then explains the products and the coulometry is in agreement.

The other oxidations are more complicated in that some of the initial cleavage products are also oxidized at these potentials. A suitable scheme for benzhydryl phenyl ketone would invoke oxidative cleavage leading to benzhydrol and benzoic acid. The benzhydrol would, however, be converted to benzophenone. This proposal is supported by the change in products observed

$$Ph_2CH\text{-}CO\text{-}Ph \xrightarrow{-2e^-} Ph_2\overset{+}{C}H + Ph\overset{+}{C}O$$

$$Ph\overset{+}{C}O \xrightarrow{H_2O} PhCO_2H + H^+$$

$$Ph_2\overset{+}{C}H \xrightarrow{H_2O} Ph_2CHOH \xrightarrow{-2e^-} Ph_2CO + 2H^+$$

when 50 mmole of methanol are added. Methanol is not being oxidized under these conditions, but will scavenge cations. The formation of benzhydryl methyl ether from diphenylacetaldehyde and diphenylmethyl phenyl ketone is supporting evidence for the intermediacy of benzhydryl cations in at least a part of the oxidation. The yield of benzhydryl methyl ether cannot be high since it also oxidizes under these conditions to benzophenone.[10]

Other pathways which could intercede involve oxidation of enols or side chain hydroxylation preceeding cleavage. The present data do not exclude a portion of the products being formed via either of these pathways and careful studies will be required to elucidate the detailed mechanism. It is clear, however, that cleavage of the benzyl-acyl bond occurs in all these reactions. The mass spectrum of each of these compounds (1) similarly has the base peak resulting from such fragmentation. Although there should be a close analogy between mass spectrometry and solution phase oxidations, fragmentation reactions of the type reported here have not been previously discovered in solution. Revelation of the similarities in these two processes should present an interesting and useful undertaking.

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8. The intermediacy of highly reactive dications cannot be dismissed.
9. The negligible yields of acetamides were unexpected. It appears that this is due in part to the presence of sodium carbonate and rather selective carbonium ion intermediates. The sodium carbonate will eventually liberate water when it reacts with acid.
10. The oxidative fragmentation of a variety of other benzylic substituents will be reported upon separately.