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ELECTRON-TRANSFER OXIDATION OF DIOXENES. AN EXAMPLE OF RADICAL CATION DISPROPORTIONATION

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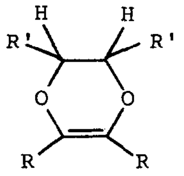
Abstract: Tris(p-bromophenyl ammoniumyl) tetrafluoroborate induces an easy electron-transfer process on dioxenes leading quantitatively to the corresponding α-diketones. A mechanism involving the disproportionation of the intermediate radical cations is discussed.

Radical cations are the well ascertained key intermediates in the photosensitized oxidation of a number of unsaturated substrates. According to the Foote[1] mechanism, radical ions form upon an electron-transfer from the substrate to the singlet excited sensitizer; the sensitizer radical anion then reduces molecular oxygen to superoxide anion which finally reacts with the substrate radical cation.

However other modes of evolution of the primary intermediate radical ions can be thought which might suitably explain such oxidation reactions mediated by electron transfer. Schaap and coworkers,[2] discussing the photooxidation of dioxenes in the presence of 9,10-dicyanoanthracene DCA as sensitizer in terms of the Foote mechanism, suggested that even a chain mechanism, involving disproportionation of the dioxene radical cations, is conceivable on the basis of thermodynamic considerations.

In the present report we provide clear chemical and spectroscopic evidence for disproportionation of dioxenes 1a-c[3] in the chemical oxidation of these substrates with tris(p-bromophenyl ammoniumyl) tetrafluoroborate 2.[4]



$(p\text{-}BrC_6H_4)_3N^{+\cdot}\ BF_4^-$

2

1a R = C_6H_5 ; R' = H

1b R = p-MeOC_6H_4 ; R' = H

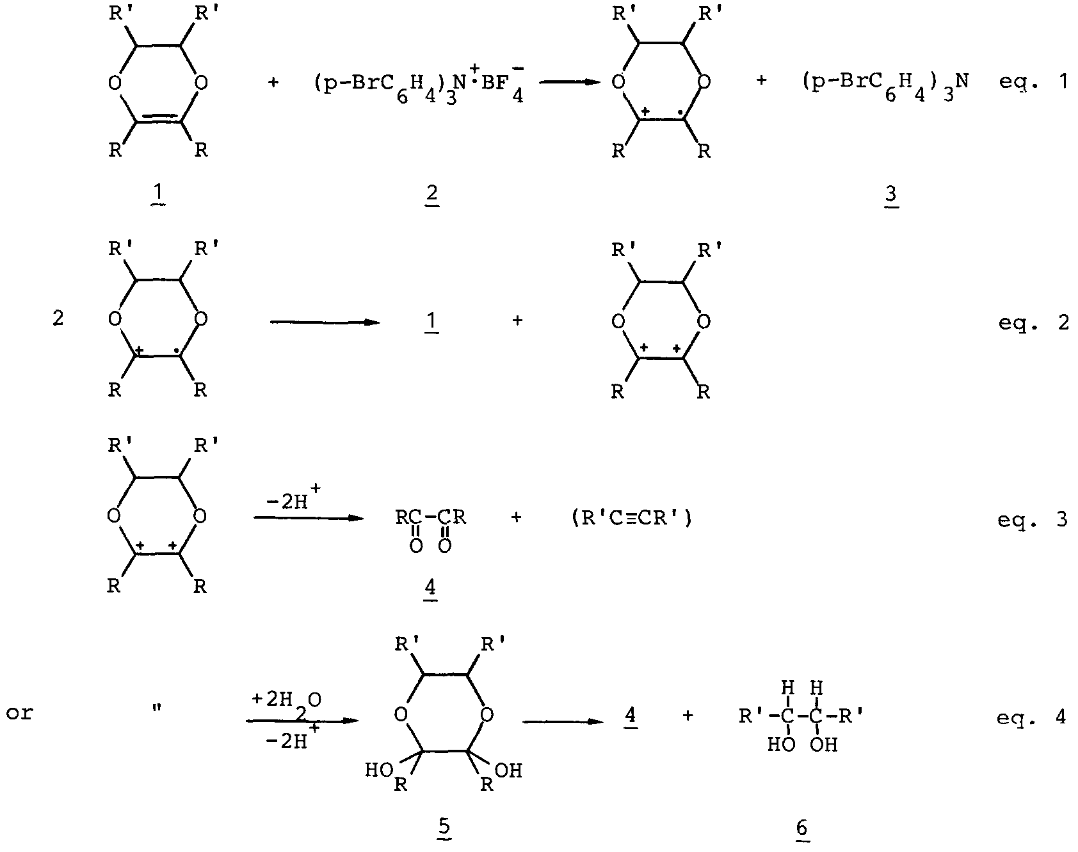
1c R = R' = C_6H_5

Treatment of a dry acetonitrile solution of 1a,b (10^{-2}M) whith one equivalent of 2, at room temperature under nitrogen or air atmosphere, gave a dark red solution which faded within a few minutes. Analysis of the colourless reaction mixtures revealed tris(p-bromophenyl)amine 3, unreacted 1a,b and benzil 4a,b in the following proportion 1:0.5:0.5. All products were isolated and characterized by NMR spectroscopy and comparison with authentic samples.
Complete conversion of the starting dioxenes 1a,b to the corresponding benzil required two equiv. of 2 .

ESR spectroscopy confirmed that, also in our experimental conditions, radical cations $1a,b^{+\cdot}$ are initially formed. The addition of one equiv. of 1a,b to an acetonitrile solution of 2 at room temperature caused the replacement of the ESR signal of radical cation 2 with a broad singlet shifted at higher field.[6] This new resonance due to $1a,b^{+\cdot}$ decreased with fading of the dark red solution and the decay appeared to be second order in $1^{+\cdot}$.

Further valuable information on the mechanism of the present reaction was obtained by following the reaction of 1a with 2 in molar ratio in deuterochloroform directly in a NMR test tube. Recording the spectrum immediately after mixing of the reactants, we observed the formation of 3 and 4a together with the complete disappearance of the singlet at 4.33δ due to the dioxene and the presence of a new broad signal at 4.00δ . After 15 min. the broad signal at 4.00δ disappeared and, most interestingly, the singlet of the starting material became again evident.

The stoichiometric requirement of two equiv. of the one-electron oxidizing agent 2, the complete disappearance of the starting material followed by its reappearance during the course of reaction, when a molar ratio 1:1 is employed, and the apparent second order decay of the radical cation $1^{+\cdot}$ are straightforward evidence that, under our experimental conditions, radical cation $1^{+\cdot}$ disproportionates to give dication species and neutral substrate as indicated in eq.2 of the scheme.



According to this scheme, benzil might derive directly from fragmentation of the dioxene dication (eq.3) and, in this case, acetylene would be formed as complementary fragment. However, attempted identification of the postulated acetylenic fragment by carrying out an oxidation reaction of tetraphenyl dioxene 1c under the same experimental conditions failed as only mesohydrobenzoin 6b (R'=Ph) was found to accompany benzil in the reaction mixture. The formation of compound 6b, instead of the expected diphenylacetylene, is accounted for by eq.4: the dioxene dication could easily be trapped by adventitious water forming dihydroxydioxane 5 which subsequently decomposes to give benzil and 6. In this connection, it is worth noting that 2,3-diethoxy-2,3-diphenyldioxane[7] was isolated from a reaction of 1a with 2 carried out in the presence of ethanol.

Work is in progress to define the scope and the mechanism of this reaction mainly as far as the role of nucleophiles on the disproportionation equilibrium is concerned.

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References and Notes

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