Cation Radicals. XXVIII. Isolation and Some Reactions of Dibenzodioxin Cation Radical Perchlorate (1)
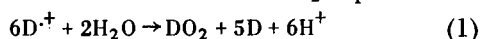
Henry J. Shine* and Lewis R. Shade

Department of Chemistry, Texas Tech University, Lubbock, Texas 79409

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Preparation and isolation of dibenzodioxin cation radical perchlorate (2) by oxidation of dibenzodioxin in ethyl acetate-lithium perchlorate at a platinum anode has been achieved. Reasonably pure 2 in amounts of 150-200 mg. were obtained reliably and reproducibly. Reaction of 2 with both nitrite and nitrate ions gave 2-nitrodibenzodioxin (3). Reaction of 2 with pyridine gave N-(2-dibenzodioxinyl)pyridinium perchlorate (4). Reaction with water gave, as anticipated, the stoichiometric amount of dibenzodioxin. Reaction with ammonia, propylamine, t-butylamine, and cyanide ion also gave dibenzodioxin with no evidence that nucleophilic substitution had occurred. It is believed that the formation of 3 and 4 represent the first examples of nucleophilic substitution into dibenzodioxin via its cation radical.

The dibenzodioxin cation radical (1) has been well characterized by esr spectroscopy, not only in concentrated sulfuric acid, (2,3) and trifluoromethane sulfonic acid (4), but also after anodic formation in acetonitrile (5) and chloroform acetonitrile (6). Cauquis (7) has studied the anodic oxidation of dibenzodioxin in acetonitrile thoroughly and has shown that 1 so formed reacts with water in the solution according to the stoichiometry of equation 1. Here, D represents dibenzodioxin and DO_2 represents dibenzodioxin-2,3-quinone, and the overall reaction of equation 1, therefore, is identical in form with that found for the perylene cation radical by Ristagno and Shine (8).

$$6D^{\cdot +} + 2H_2O \rightarrow DO_2 + 5D + 6H^+ \qquad (1)$$

Ueda has noted that the colors formed by (and used for qualitatively identifying) dibenzodioxins in concentrated sulfuric acid are dispelled by the addition of water, and has implied (i.e., by specific reference to the blue color from 1,6-dibromodibenzodioxin) that the water reaction regenerates a dibenzodioxin quantitatively (3). In view of later knowledge (7,8), quantitative (i.e., 100%) regeneration of a dibenzodioxin from its cation radical is not correct, but, as with the perylene system (8,9), it is not surprising that small amounts of quinones formed in sulfuric acid could be overlooked. As far as we are aware, the reaction with water (7) is all that has been reported about the chemistry of 1. In contrast, the chemistry of analogous thianthrene and phenothiazine cation radicals has received a lot of attention (10). We set out, therefore, to isolate the solid perchlorate (2) of 1 and to study its reactions in homogeneous solution.

Cauquis had already noted that small amounts of 2 were deposited on the anode in the oxidation of concentrated

solutions of dibenzodioxin in acetonitrile-lithium perchlorate at -10°. The solid could be kept in the atmosphere for several hours without appreciable change. We found that in our hands this technique gave irreproducible amounts of 2 far too small for our use. Parker (11) has reported that cation radical salts, e.g., of thianthrene, can be prepared by electrolysis in trifluoroacetic acid without inclusion of a supporting electrolyte. We found that electrolysis of dibenzodioxin in this way gave very stable solutions of the cation radical (1). Unfortunately, dibenzodioxin is poorly soluble in trifluoroacetic acid so that only small amounts of 1 could be obtained in solution. Furthermore, the cation radical trifluoroacetate left by evaporation of the trifluoroacetic acid decomposed soon afterwards. The salt could be precipitated in small amounts by pouring the acid solution into dry ether, but again decomposition occurred once the blue solid was collected. Search for more fruitful conditions of anodic oxidation led to acetic anhydride and, finally, ethyl acetate as solvents. Each of these dissolves dibenzodioxin and lithium perchlorate well enough to make electrolysis practical. Ethyl acetate gave the better results, however. Eventually, routine preparation of 150-200 mg amounts of solid 2, deposited on a platinum foil anode, was achieved.

Each preparation of 2 was analyzed for cation radical content iodimetrically before use and was found to contain 85-90% of 2. Part of the remaining 10-15% was found to be dibenzodioxin by preparative-scale reduction with iodide ion followed by quantitative isolation of the dibenzodioxin by tlc. The assay of dibenzodioxin (by ultraviolet spectroscopy) was always greater than required by the 2 in the sample, indicating that the sample contained dibenzodioxin. Analogous experience was encountered with
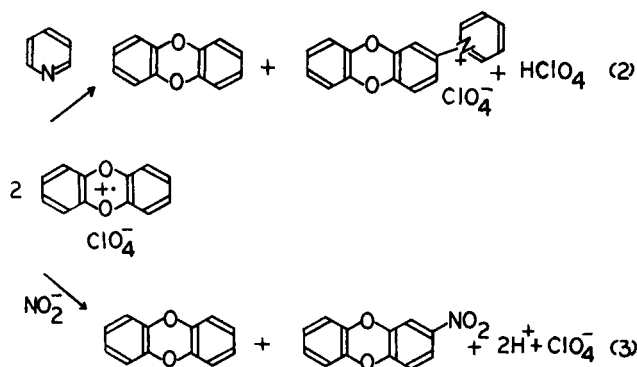
electrochemical preparations of perylene cation radical perchlorate (8). We were never able to account for the balance of the impurity in our samples of 2.

Storage of 2 in the desiccator was accompanied by decomposition, and one of the products of decomposition was dibenzodioxin dimer, m.p. 230-231°. The dimer was detected by tlc in only small amounts in newly-prepared samples of 2. Therefore, the solid was used for reactions with nucleophiles immediately after assay was complete.

The anodic preparation and isolation of solid cation radical salts is uncommon. Isolation of the perchlorates of the perylene cation radical (8,12) and the o-tolidine cation radical (13) have been reported. As far as we are aware 2 has not, until now, been obtainable, reproducibly and reliably, either anodically or chemically in amounts usable for chemical studies.

Reaction of 2 with water in acetonitrile gave dibenzodioxin, as described by Cauquis (7). Cauquis noted that the other anticipated product, dibenzodioxin-2,3-quinone (eq. 1), underwent *in situ* cleavage reactions. Like Cauquis, we were unable to identify the quinone itself, although tlc showed the presence of small amounts of products besides dibenzodioxin.

Pyridine reacted with 2 to give N-(2-dibenzodioxinyl)-pyridinium perchlorate (4). Nitrite ion also reacted as a nucleophile with 2 forming 2-nitrodibenzodioxin. (3). In each of these reactions dibenzodioxin was also formed in amounts consistent with equations 2 (pyridine) and 3 (ni-

trite ion). These reactions follow the pattern of analogous thianthrene- and phenothiazine cation radical reactions (10), and whether or not the dibenzodioxin cation radical or dication is involved cannot yet be said. We believe however that these two examples are the first successful substitutions into the dibenzodioxin nucleus *via* its cation radical.

The nitro compound 3 was also formed from reaction of 2 with nitrate ion. Indeed, in solvent nitromethane 3 was the only product; *i.e.* dibenzodioxin was not also obtained. The mechanism of this unusual reaction is not yet known. Nitric acid nitration of dibenzodioxin gives 3 (14), and it may be thought that in the nitrate ion reaction, poorly

nucleophilic nitrate ion is converted into nitric acid by, first, electron transfer to 1 and next, abstraction of solvent hydrogen atom by nitrate radical. A pathway like this, in which nitrate ion is oxidized anodically, has been encountered in anodic reactions of other compounds (15). However, electron transfer between 1 and nitrate ion is most unlikely since the half-wave potential $(E_{1/2})$ for dibenzodioxin is 1.09v (7) and for nitrate ion is 1.76v (16), so that nitric acid nitration in the present reaction does not seem a reasonable possibility.

Reaction of 2 with other nitrogen-containing nucleophiles (cyanide ion, ammonia, propylamine and t-butylamine) did not lead to substitution, but gave dibenzodioxin in high yield. Here again the problem of the electron transfer is encountered. Electron transfer from cyanide ion, $E_{1/2}$ = 0.66v (17), to 1 would not be unreasonable. On the other hand the half-wave potentials of the amines (18) are high enough to make electron transfer to 1 most unlikely. The cause of the reduction of 1, therefore, remains unknown, but it is apparent that the four nucleophiles are insufficiently nucleophilic for substitution to compete with the (unknown) reduction of the cation radical. The complexity of these factors is accentuated by the successful substitutions by pyridine, $E_{1/2}$ = 1.82v (18), and nitrite ion, $E_{1/2} \cong 0.70$ (19,20).

EXPERIMENTAL

Dibenzodioxin was prepared by Tomita's method (21) as modified by Gilman and Dietrich (22), and ourselves. A mixture of o-chlorophenol (136 g., 1.05 moles), dry potassium carbonate (73 g., 0.53 mole), and copper powder (8 g.) was heated for 6 hours at 170-180° in an oil bath. The tarry mixture was next refluxed with aqueous potassium hydroxide and extracted with ether. Evaporation of the ether gave a yellow-brown residue from which the yellow impurity could not be removed by chromatography on alumina as described earlier (16). Consequently, the discolored solid was heated under vacuum in a Claisen flask submerged in an oil bath so that colorless dibenzodioxin sublimed and distilled into a receiver. Crystallization from ethanol gave dibenzodioxin in yields of 10% and less, m.p. 120-121°. Subsequently, a gift of crude dibenzodioxin was given to us from the residues of the large-scale manufacture of dibenzodioxin (23). The crude black material was extracted with ether and after washing the ether solution with aqueous potassium hydroxide it was treated as above.

Dibenzodioxin Cation Radical Perchlorate (2).

After many trials with acetonitrile, trifluoroacetic acid, and other solvents, ethyl acetate and the following procedure were chosen as the most productive. Dibenzodioxin (500 mg.) and lithium perchlorate (6 g.) were dissolved in 200-250 ml. of reagent-grade ethyl acetate. A copper cathode was placed in a Soxhlet thimble (43 mm x 123 mm) suspended within a cylindrical platinum anode (dia. 45 mm, height 50 mm, thickness 1.25 mm). Electrolysis was carried out in an open beaker at a controlled potential of 1.2 V *vs.* Ag-AgClO₄ (24). A blue solid appeared on the anode as soon as electrolysis was begun. After 1-1.5 hours the anode was removed and washed in ethyl acetate. The blue deposit was removed by gentle scraping and dried under vacuum. Electrolysis for longer periods was found to give less pure 2.

The amount of **2** in the blue deposit was assayed by adding a weighed sample (10-20 mg.) to a solution of tetrabutylammonium iodide in dry acetonitrile and titrating the liberated iodine potentiometrically. The blue solid usually contained 85-90% of **2**. In order to discover the nature of the remaining material larger samples (250 mg.) of the blue solid were reduced with iodide ion as described. Water (0.5 ml.) and sodium thiosulfate were added to the solution which was stirred to remove iodine. After filtration the solution was made up to the mark in a 100-ml. volumetric flask and 10-ml. aliquots were used for quantitative tlc on silica. Development with 30-60° petroleum ether gave dibenzodioxin and two other bands. The dibenzodioxin band (second from solvent front) was removed and extracted with cyclohexane, and the dibenzodioxin content was determined by uv spectroscopy. Each of the other two bands contained a greasy material which could not be identified. The presence of a dibenzodioxin dimer in the band with lowest R_f was indicated by a peak for mass 366 in the mass spectrum.

Samples of blue solid which had been stored in the desiccator from 1 to 4 days were found to contain only 20-65% of **2**. From one such sample a considerable amount of white solid, m.p. 230-231° (ethanol), parent mass 366, was isolated, and was apparently a dimer of dibenzodioxin.

Reaction of 2 with Nitrite Ion.

To a stirred suspension of dry sodium nitrite in acetonitrile was added 182 mg. (0.537 mmole) of **2**. The blue color of **2** was discharged, and tlc of the yellow solution on silica (n-pentane) showed two spots. The solution was filtered, diluted to 100 ml. and tlc was carried out quantitatively on 10-ml. portions. Each band was removed from the plate and extracted with methylene chloride. The first band (highest R_f) was shown by ultraviolet spectrum to be dibenzodioxin and the second to be **3**. Assay by ultraviolet spectroscopy gave 47% of dibenzodioxin (94% of theory) and 50% of **3** (100% of theory). Evaporation of the solution of **3** gave a yellow solid, m.p. 148-149° (aqueous ethanol). An authentic sample of **3** had m.p. 144-146° (14).

Reaction of 2 with Nitrate Ion.

Reaction was carried out as above. Quantitative tlc and ultraviolet assays gave 31% of dibenzodioxin and 54% of **3**. Two additional bands were developed on the plate with acetone after initial development with pentane, but attempts to identify the small amounts of material in these bands failed.

When reaction of 297 mg. (0.907 mmole) of **2** was carried out in nitromethane only one major tlc band was obtained, which was shown to contain **3**; dibenzodioxin was not detected. Assay of the **3** gave 1.01 mmoles (112%). A second, similar, reaction was worked up by column chromatography. After evaporation of the nitromethane the residue was dissolved in benzene and chromatographed on silica gel with benzene. The product had m.p. 148-149° (aqueous ethanol).

Reaction of 2 with Pyridine.

One ml. of pyridine was added to a solution of 315 mg. (0.985 mmole) of **2** in acetonitrile, resulting in a yellow-brown solution and a precipitate. The mixture was evaporated to dryness under vacuum and the residue was washed several times with methylene chloride. Not all of the residue dissolved. Quantitative tlc of the methylene chloride solution gave 0.52 mmole (106% of theory) of dibenzodioxin. The methylene-chloride insoluble material was washed several times with water and dried giving 167 mg. (94% of theory) of crude **4**. More of **4** was prepared by larger-scale reactions. Crystallization from aqueous acetonitrile gave m.p. 348-350° dec. λ max 343 nm (ε, 3.06 x 10³) and 260 (1.2 x 10⁴).

Anal. Calcd. for $C_{17}H_{12}O_2NClO_4$: C, 56.5; H, 3.32; N, 3.88;

Cl, 9.79. Found: C, 56.4; H, 3.70; N, 4.22; Cl, 9.11.

Reactions with other nucleophiles were carried out analogously. Ammonia, propylamine, t-butylamine, and cyanide ion gave dibenzodioxin as the only identifiable product. Reaction with azide ion gave a mixture of products, none of which could be separated and identified.

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