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Decomposition of 1,4-Dimethoxybenzene Radical Cations in CH_3NO_2-$AlCl_3$ System[1)]

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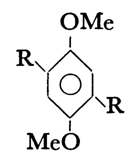
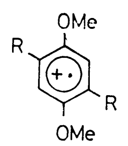
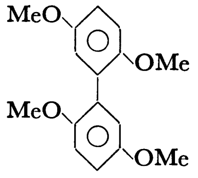
Synopsis. The decomposition of 1,4-dimethoxybenzene cation (**2a**) and 1,4-dimethoxy-2,5-dimethylbenzene cation (**2b**) gave 2,2′,5,5′-tetramethoxydiphenyl and 2,5-dimethyl-*p*-benzoquinone indicating that the reaction pathway depends on substituent at nucleus of the radical cations **2**.

In a previous work,[1)] we reported that 1,4-dialkoxybenzenes are rapidly oxidized in various nitro compounds in the presence of $AlCl_3$ quantitatively to form fairly stable corresponding radical cations.[1,2)] In the CH_3NO_2–$AlCl_3$ system, however, they slowly decompose on being left to stand at room temperature. The initial step of oxidation of alkoxybenzenes has been considered to be radical cation formation,[3–5)] but the reaction of actual alkoxybenzene radical cations is little known. The chemical reactions of several stable radical cations, such as those from perylene,[6)] thianthrene,[7)] and aromatic amines[8)] have been reported. The present paper reports on the decomposition of 1,4-dimethoxybenzene radical cations in the CH_3NO_2–$AlCl_3$ system predominantly giving a dimerized product or quinoid compound depending on the substituent at nucleus of the radical cations.

When solutions of radical cations **2** quantitatively generated by dissolving **1** in CH_3NO_2–$AlCl_3$ sytsem were allowed to stand at room temperature, the radical cations slowly deteriorated with fading of the initial deep green color of **2**. **1a** (34%) and dimer **3** (39%) were isolated from decomposition products of **2a** and **1b** (45%), **4** (14%), and small amounts of **5** from those of **2b**. The products except for the starting materials (**1**) were not obtained from the solution of **1** in CH_3CN–$AlCl_3$, CH_2Cl_2–$AlCl_3$, or CH_3NO_2 alone where no **2** is formed, indicating that the products resulted from **2**.


1a : R=H
b : R=Me


2a : R=H
b : R=Me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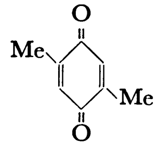
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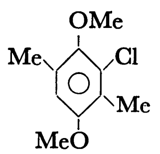
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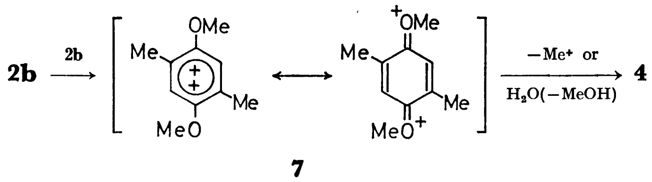
The formation of **3** from **2a** provides a direct evidence for the proposed radical cation mechanism for the oxidation of methoxybenzenes to give such dimerized products (Scholl reactions).[5,9)]

In the case of **2b**, neither the dimer of type **3** nor one dimerized at the methyl carbon such as that formed in the reaction of 9,10-dimethylanthracene radical cation in which the highest spin density is at the methyl carbon[10)] was obtained, suggesting that the reaction path way is largely affected by the substitution of radical cations. It seems likely that coupling at the 3 and 6 positions in **2b** is hampered by the steric effects of the flanking groups, and coupling at the methyl group is put away by disproportionation to give the corresponding dication **7** which can be brought by the stabilizing effects of lone pairs in the 1,4-dimethoxy groups, and gives **4** either by leaving methyl cation or by reaction with water in working-up of the reaction mixture. Compound **5** is considered to form by chlorination of **1b** reformed in a secondary reaction since the amount of **5** increases by longer standing of the reaction mixture with decrease in the yield of **1b**.



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Experimental

Formation and Decomposition of **2**. To a solution of **1** (5 mmol) in CH_3NO_2 (50 ml) was added anhydrous $AlCl_3$ (1.33 g) under anhydrous atmosphere. The solution immediately assumed a green color due to the quantitative formation of **2** as determined by ESR. After the solution had been left to stand at room temperature for 1 hr, the mixture was poured into excess amount of ice-water and extracted with ether. The ether extract was washed (water), dried (Na_2SO_4), evaporated and chromatographed.

The separation of the products from **2a** by tlc (silica gel) developing with C_6H_6 gave **1a** (0.23 g) and **3**,[11)] mp 113—114 °C (0.265 g).

The products from **2b** were chromatographed on a silica gel (50 g) column. Elution with benzene gave **2a** (0.37 g), **5**, colorless plates, mp 135—137 °C (small amounts), and **4**, mp 121—122 °C (0.01 g) identified with authentic samples.

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