

Decomposition of 1,4-Dimethoxybenzene Radical Cations in $\text{CH}_3\text{NO}_2\text{-AlCl}_3$ System¹⁾

Akira NISHINAGA, Hidetoshi HAYASHI, and Teruo MATSUURA

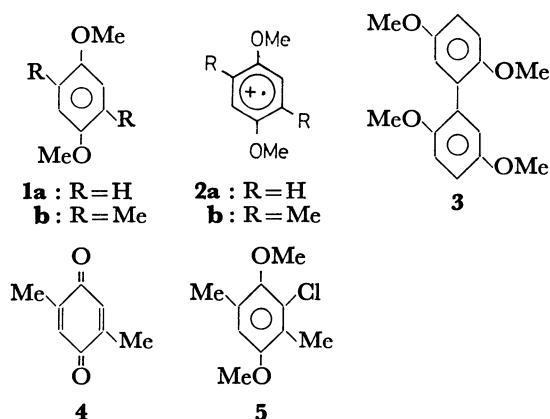
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606

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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 $\text{CH}_3\text{NO}_2\text{-AlCl}_3$ 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 amines⁸⁾ have been reported. The present paper reports on the decomposition of 1,4-dimethoxybenzene radical cations in the $\text{CH}_3\text{NO}_2\text{-AlCl}_3$ 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 $\text{CH}_3\text{NO}_2\text{-AlCl}_3$ system 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

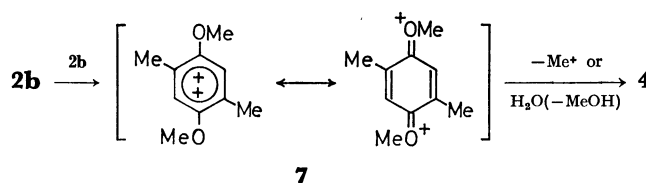


of **2b**. The products except for the starting materials (**1**) were not obtained from the solution of **1** in $\text{CH}_3\text{CN-AlCl}_3$, $\text{CH}_2\text{Cl}_2\text{-AlCl}_3$, or CH_3NO_2 alone where no **2** is formed, indicating that the products resulted from **2**.

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-dimethylantracene radical cation in which the highest spin density is at the methyl carbon¹⁰⁾ was obtained, suggesting that the reaction pathway 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 chlo-



ration 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**.

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.

References

- 1) Aromatic Radical Cations IV. Part III: A. Nishinaga, H. Hayashi, and T. Matsuura, *Chem. Lett.*, **1973**, 141. Preceding papers: A. Nishinaga, P. Ziemek, and T. Matsuura, *Tetrahedron Lett.*, **1969**, 4905; *J. Chem. Soc.*, **1970**, 2613.
- 2) W. F. Forbes and P. D. Sullivan, *J. Amer. Chem. Soc.*, **88**, 2862 (1966).
- 3) A. Zweig, W. G. Hodgson, and W. H. Jura, *ibid.*, **86**, 4124 (1964).
- 4) P. J. Andrusis, Jr., M. J. S. Dewar, R. Dietz, and

R. L. Hunt, *J. Amer. Chem. Soc.*, **88**, 5473, 5483 (1966).

5) O. C. Musgrave, *Chem. Rev.*, **69**, 499 (1969).

6) C. V. Ristagno and H. J. Shine, *J. Amer. Chem. Soc.*, **93**, 1811 (1971); *J. Org. Chem.*, **36**, 4050 (1971).

7) H. J. Shine, C. F. Dais, and R. J. Small, *J. Org. Chem.*, **29**, 21 (1964); Y. Murata and H. J. Shine, *ibid.*, **34**, 3368 (1969); J. J. Silber and H. J. Shine, *ibid.*, **36**, 2923 (1971); H. J. Shine and Y. Murata, *J. Amer. Chem. Soc.*, **91**, 1872 (1969); V. D. Parker and L. Eberson, *ibid.*, **92**, 7488 (1970); H. J. Shine and J. J. Silber, *ibid.*, **94**, 1026 (1972); H. J. Shine and L. Piette, *ibid.*, **84**, 4798 (1962).

8) A. Ledwith, *Accounts Chem. Res.*, **5**, 133 (1972) and references cited therein; P. Bruni, M. Colonna, and L. Greci, *Tetrahedron*, **27**, 5893 (1971).

9) A. T. Balaban and C. D. Nenitzescu, "Friedel-Crafts and Related Reactions," Vol. II, Part 2, ed. by G. A. Olah, Interscience Publishers, New York, N. Y. (1964), p. 979.

10) V. D. Parker and L. Eberson, *Tetrahedron Lett.*, **1969**, 2839.

11) P. Kovacic and M. E. Kurz, *J. Org. Chem.*, **31**, 2011 (1966).
