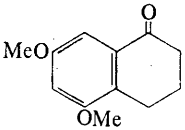
A Convenient Synthesis of 1,2,3,4-Tetrahydro-5,7-dimethoxy-1-oxonaphthalene

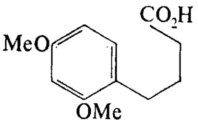
By P. NARASIMHA RAO

(*Division of Biological Growth and Development, Southwest Foundation for Research and Education, San Antonio, Texas* 78206)

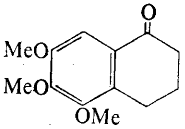
IN connection with some projected synthetic work, we were interested in the preparation of 1,2,3,4-tetrahydro-5,7-dimethoxy-1-oxonaphthalene (I). An obvious method for its preparation appeared to be the cyclization of 3-(2,4-dimethoxyphenyl)-butyric acid (II). Davies *et al.*[1] attempted this and found it was difficult to cyclize the acid (II) and could obtain the tetralone (I) in 4—6% yield only. This could easily be explained by the strong deactivating influence by the two methoxy-groups at the *meta*-position.



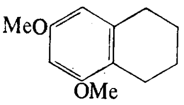
(I)



(II)



(III)



(IV)

Kuehne and Lambert[2] observed that when 3,4,5-trimethoxybenzoic acid or its amide were reduced with sodium in liquid ammonia, the 4-methoxy-group was selectively removed and the corresponding 1,4-dihydro-3,5-dimethoxy-products resulted in good yield. It occurred to us that by controlled reduction with sodium in liquid ammonia, it might be possible to demethoxylate 1,2,3,4-tetrahydro-5,6,7-trimethoxy-1-oxonaphthalene [(III), available in excellent yield by use of the method of Haworth *et al.*[3]], selectively at C-6, without reducing the aromatic ring. The dimethoxy-ketone (I) could in fact be obtained from (III) in 40—45% yield. To a solution of (III) (5 g., 0·02 mol.) in tetrahydrofuran (30 ml.) and liquid ammonia (400 ml), sodium (3·66 g., 0·15 g. atoms) was added, and the reaction was allowed to proceed for exactly ten minutes. Excess sodium was then decomposed by the addition of ammonium chloride. Chromatographic separation of the reaction mixture on alumina gave 1,2,3,4-tetrahydro-5,7-dimethoxynaphthalene (IV), (2%), m.p. 36—37·5°; δ†3·76 (6H, 2 OMe), 6·02 and 6·03 p.p.m. (both 1H, d, *J* 2 Hz., *m*-coupled aromatic), 1,2,3,4-tetrahydro-5,7-dimethoxy-1-oxonaphthalene (I), (43%), m.p 67–68°; δ 3·85 (6H, 2 OMe), 6·61 and 7·13 p.p.m. (both 1H, d, *J* 3 Hz., *m*-coupled aromatic), starting material (III), (5%), m.p. 74—75° and finally a more polar fraction (*ca.* 35%). This polar fraction was not investigated in detail, but the n.m.r. spectrum indicated that the aromatic ring was reduced and further loss of methoxyl functions occurred.

By prolonging the reaction for more than ten minutes or increasing the sodium concentration, the yield of (I) was decreased and the amount of polar fraction increased. If the sodium was decreased very little dimethoxy-compound was formed and most of the starting material was recovered. Use of lithium instead of sodium in the reaction did not significantly change the ratio of the reaction products.

The small amount of 5,7-dimethoxytetralin (IV) obtained from the reaction mixture apparently resulted from the reduction of carbonyl function and subsequent hydrogenolysis of the benzylic alcohol in liquid ammonia and sodium.

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† δ measured in $CDCl_3$ with tetramethylsilane as internal standard, throughout.

[1] J. E. Davies, F. E. King, and J. C. Roberts, *J. Chem. Soc.*, 1955, 2782.
[2] M. E. Kuehne and B. F. Lambart, *J. Amer. Chem. Soc.*, 1959, 81 4278.
[3] R. D. Haworth, B. P. Moore, and P. L. Pauson, *J. Chem. Soc.*, 1949, 3271.