Acidic Cleavage of Anispinacolone. Formation of a Substituted Benzofuran *via* an Acylcarbonium Ion Intermediate

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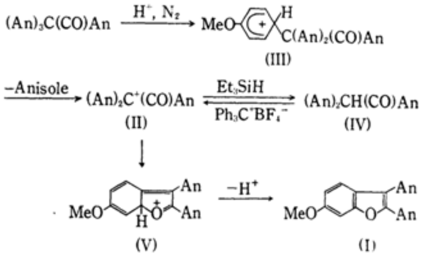
The acidic cleavage of anispinacolone (ω,ω,ω-tris(*p*-methoxyphenyl)-*p*-methoxyacetophenone) in 1,2-dichloroethane has been studied by Buckles and his collaborators;[1] the major product has been identified as the tris(*p*-methoxyphenyl)methyl cation on the basis of the visible and IR spectra of the reaction mixture. Following their method, we have found that this cleavage is accelerated by the interaction of molecular oxygen and proceeds *via* a radical (presumably a cation radical) intermediate; we have ascertained this by studying the ESR spectrum of the reaction mixture.[2]

In contrast, we will now show that, under an atmosphere of nitrogen or in an evacuated system, the acidic cleavage of the titled compound proceeds in an unexpected way, affording 2,3-bis(*p*-methoxyphenyl)-6-methoxybenzofuran (I) and anisole.

A 0.1 M solution of anispinacolone in 1,2-dichloroethane was allowed to react with twenty molar equivalents of trifluoroacetic acid in a sealed tube filled with nitrogen at 50°C for 24 hr; the reaction mixture was then washed with an aqueous alkaline solution, from which a small amount of anisic acid (4.2%)[3] was later isolated. After the usual working-up of the remaining organic layer and subsequent chromatography over silica gel, we isolated anisole (40%), the substituted benzofuran I (87%), tris(*p*-methoxyphenyl)carbinol (4.5%), and small amount of unchanged anispinacolone (9.0%).

In view of the facile elimination of *m*-dimethoxybenzene from 2,6,2′,6′,2″,6″-hexamethoxytriphenylmethane in dichloromethane in the presence of trifluoroacetic acid,[4] it is most probable that an acylcarbonium ion (II) would be formed as a result of the facile elimination of anisole from anispinacolone, protonated on its *p*-methoxyphenyl group (III).



(An = *p*-methoxyphenyl)

In order to trap the supposed acylcarbonium ion II, the acidic cleavage was carried out in the presence of a hydride donor, *i. e.*, triethylsilane,[4] with the reaction conditions being otherwise the same as above; ω,ω-bis(*p*-methoxyphenyl)-*p*-methoxyacetophenone (IV) (85%) and anisole (75%) were isolated, along with a small amount of I (3.4%), by elution chromatography over silica gel. This indicates that the acylcarbonium ion II is a common precursor to IV and I.

The intramolecular cyclization of the acylcarbonium ion II to the substituted benzofuran I was confirmed by the fact that, when the ketone IV was treated with two molar equivalents of triphenylmethyl tetrafluoroborate in 1,2-dichloroethane at 50°C for 22.5 hr, I was obtained in a 3.7% yield *via* II, produced by hydride abstraction from IV. The other compounds isolated from the reaction mixture were triphenylmethane (2.2%) and unchanged ketone IV (95%); they were obtained after the usual working-up and after subsequent t.l.c. separation over silica gel. This cyclization conceivably proceeds *via* a substituted 1-oxonia-7a*H*-indene (V).[5]

Experiments with other substituted benzopinacolones are under way in order to clarify the scope of this novel reaction.

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[1] R. E. Buckles, R. E. Erickson, J. D. Snyder and W. B. Person, *J. Am. Chem. Soc.*, **82**, 2444 (1960).

[2] The details will be reported elsewhere.

[3] Satisfactory analytical data (mixed melting points, elemental analyses, NMR and IR spectra) have been secured for all the products described in this communication.

[4] F. A. Carey and H. S. Tremper, *J. Am. Chem. Soc.*, **90**, 2578 (1968).

[5] For a substituted 1-oxoniacyclopentene, see C. U. Pittman, Jr. and S. P. McManus, *Chem. Commun.*, **1968**, 1479; H. R. Ward and P. D. Sherman, Jr., *J. Am. Chem. Soc.*, **90**, 3812 (1968).