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THE DIMERIC NATURE OF THE SUPPOSED 2-P-ANISYLNORBORNENE 2,3-EXO-OXIDE

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The synthesis of 2-p-anisylnorbornene 2,3-exo-oxide (I) has recently been reported in this journal.[1] The remarkable way in which it was prepared (reaction of the corresponding diol II with 30% HCl in THF), the failure in its formation by the usual peroxyacid oxidation, its quite unusual stability, and several not fully explained pecularities in the physical data that were used for its characterization attracted our attention, because we could not reconcile the properties of I with those of other anisyl-substituted epoxides, particularly 1-p-anisylcyclohexene oxide (the analogue of I without the methylene bridge), on which we are working at present, and which are all very labile under acidic conditions. Nor did we think that hindrance to attack from the endo side alone could be responsible for its lack of reactivity, since acid-catalyzed reactions of epoxides are normally initiated by electrophilic attack on oxygen, and in the specific case of aryl-substituted epoxides the nucleophile usually enters cis to oxygen. It was also in contrast with previous work from this Institute[2] that the reaction of 2-p-anisylnorbornene with peracid to give the monoester of II should take place by direct addition of the peroxyacid to the double bond, rather than through reaction with the carboxylic acid of the epoxide, formed as an intermediate. We therefore repeated the reaction of II with acid and obtained a compound, m.p. 194-195°, obviously identical with the one reported as I. It did not react with CCl_3COOH in benzene, nor with BF_3-ether complex in benzene, even after 24 hr; other anisyl epoxides react immediately under such conditions.

We therefore investigated alternative formulations, and soon found out that the molecular weight of the compound was 432 and not 216, as required by I; this was seen both by the Rast method (in camphene, found 432 ± 5) and by mass spectrometry, which revealed a M^+ peak at m/e 432 (ca. 6% of base peak at m/e 200), that appears to have escaped the attention of the previous workers, probably because of the lack of peaks in the region of m/e 216-432. On the basis of these results the compound previously assumed to be the epoxide I is a dimer, and the most likely structure for it is IV. It is well known that diols can give dioxanes under acidic conditions and that this reaction is particularly facile when one of the hydroxyl groups is attached to a tertiary benzylic carbon.[3]

The nmr spectrum* of the compound under discussion is fully consistent with structure IV. In the aromatic proton region two of the protons appear as doublets of doublets at 7.49 and 6.94 ppm; they are coupled to each other with a J_{ortho} of ~ 8.4 cps and are further split with a J_{meta} of ~ 1.9 cps. The other two aromatic protons resonate at 6.48 ppm. This pattern is consistent with the assignments shown in III, but not with the previously proposed ones[1] (both signals at lower field were assigned to the protons meta to OCH_3). Restricted rotation of the anisyl group, which is much more likely in IV than in I, can well explain this pattern, that is quite different from the one observed with II (A,A',B,B' system, values in parentheses in III). Dreiding models show that in the least hindered conformation of IV one ortho and one meta proton on one side of each ring should fall into the shielding cone of the other ring. This explains the considerable up-field shift of two of the signals with respect to the corresponding signals of II; this effect is stronger on the ortho than on the meta proton and causes the fortuitous coincidence of their chemical shifts at 6.48 ppm. The protons on the methylene bridge resonate at 1.34 and 2.60 ppm (and not 0.74 and 2.62, as reported), with a J of 9.3 cps (double resonance). The signal for the proton α to oxygen shows up as a slightly broadened singlet ($w_{1/2}$ ~ 3 cps) at 3.54 ppm, and is consistent with the dioxane structure.[4]

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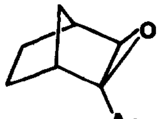
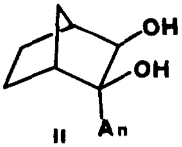
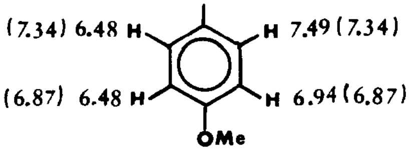
* Nmr spectra were recorded at 60 Mc/s with a JEOL C60HL instrument, in $CDCl_3$ solution. Chemical shifts are expressed in ppm (δ scale) from internal TMS.



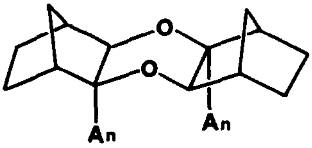
I



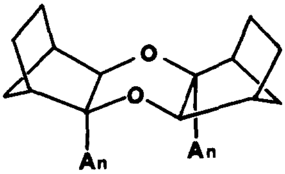
II



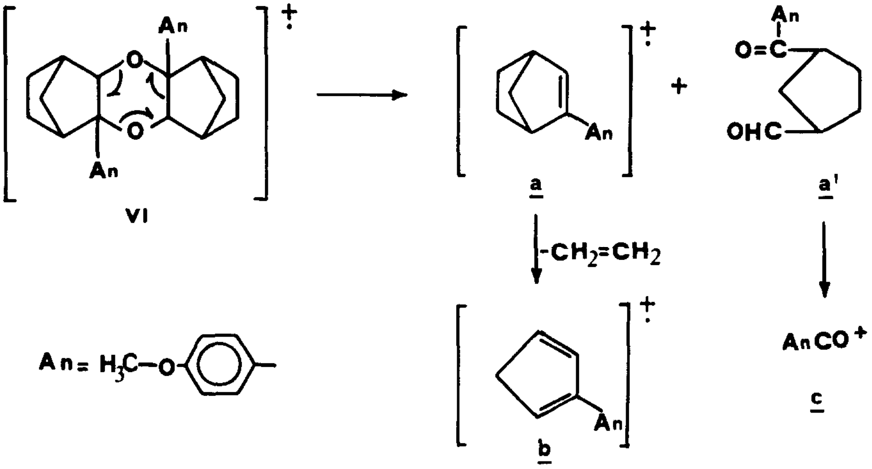
III



IV



V



The symmetry of the exo-cis-exo configuration of IV is in accordance with the simple nmr spectrum. A proof that the configuration of IV must be the same as that of II was given by a short treatment of IV with 96% H_2SO_4, followed by addition of ice; some II was obtained by preparative TLC from the reaction mixture, which also contained much unchanged IV and a trace of a ketone. This rules out the endo-cis-endo structure V.

Structure IV also agrees well with the fragmentation pattern in the mass spectrum. The base peak at m/e 200 must be due to ion a, formed as shown in VI, rather than by an unprecedented loss of oxygen from I. a gives b by a retro-Diels-Alder fission. The strong peak at m/e 135 can be ascribed to c, formed from the neutral fragment a'.

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