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PROPERTIES OF 2-ARYLNORBORNENE OXIDES AND OF THE DIMER FORMED BY DEHYDRATION OF 2-*P*-ANISYLNORBORNANE-2,3-*CIS-EXO*-DIOL

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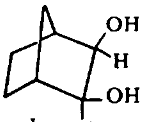
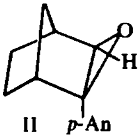
Abstract—2-Phenylnorbornene-2,3-*exo*-oxide and its *p*-chloro analog have been prepared. A thorough NMR analysis of the former compound in conjunction with its facile epoxide opening reactions prompted reexamination of an earlier structural assignment of the *p*-methoxy analog to the product formed from acid catalyzed dehydration of 2-*p*-anisylnorbornane-2,3-*cis*-*exo*-diol. The product was found to be a *p*-dioxane, a dimer of molecular weight 432. The 100 MHz NMR spectrum of the dimer recorded at 29° shows that a considerable barrier exists to rotation of the *p*-anisyl group about the bond joining it to the norbornane skeleton. Variable temperature NMR studies on a sample substituted with deuterium at the positions *ortho* to the methoxy group gave $\Delta G^{\ddagger}_{83}$ = 19·6 kcal/mole for this process.

RECENTLY[1] it was reported that acid catalyzed dehydration of 2-*p*-anisylnorbornane-2,3-*cis*-*exo*-diol(I) gave 2-*p*-anisylnorbornene-2,3-*exo*-oxide(II) as one of the reaction products. The unique properties reported for this latter compound prompted us to examine the properties of other 2-arylnorbornene-2,3-*exo*-oxides.

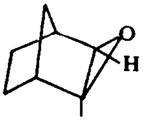


I

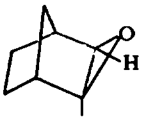


II

By Payne's procedure,[2] using benzonitrile and 50% H_2O_2 in methanol solution with added potassium bicarbonate, we have obtained 2-phenylnorbornene-2,3-*exo*-oxide(III) and the *p*-chlorophenyl analog(IV) from the corresponding alkenes. The phenyl singlet at δ 7·30 in III's NMR spectrum precludes restricted rotation about



III

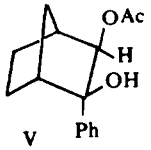


IV

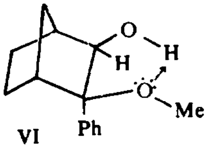
the sp^3–sp^2 bond to the aryl ring of the type reported for II. The spectrum also showed a narrow multiplet at δ 3·32 (H-3), narrow multiplets at δ 2·78 and 2·50 (H-1 and H-4), and a doublet (separation 9·5 Hz) with fine structure (doublet of triplets) at δ 0·82 (H-7*a*). The last feature can be best rationalized by $J_{1,7a} = J_{4,7a} = 1{\cdot}5$ Hz with $J_{3n,7a} = 0{\cdot}8$ Hz as expected for this system.[3] The resonance due to H-7*s* was located by a hidden-proton experiment: irradiation of the signal at δ 0·82 caused a collapse of lines in the envelope containing resonances at δ 1·62. The chemical shifts of H-7*a* and H-7*s* are only slightly downfield relative to those of norbornene-2,3-*exo*-oxide.[4] Irradiation of the signal at δ 0·82 also collapsed the H-3*n* signal at δ 3·32 to a doublet ($J_{3n,4} = 1{\cdot}3$ Hz).

The mass spectra of III and IV displayed significant P-16 peaks. Extensive atomic oxygen expulsion is not characteristic of the mass spectra of aliphatic or aromatic epoxides.[5] In III the intensities of the parent peak ($m/e = 186$) to the P-16 peak relative to the base peak ($m/e = 154$) were 22·0:8·6, while in IV the parent peak ($m/e = 222$) to P-16 peak ratio was 34·9:31·0 (base peak, $m/e = 151$). It is very unlikely that the P-16 peak is due to loss of CH_4. Neither epoxide exhibited the extensive P-16 peak reported for II.

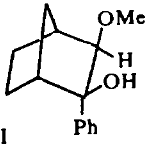
III reacted readily with acetic acid to give the hydroxyacetate V, characterized by the 3*n* proton signal at δ 5·14 (remaining assignments in experimental) and by the formation of the identical compound from acetylation of the phenyl analog of I. III reacted with methanol at room temperature to give the methoxyhydrin VI. This structure was assigned, rather than the isomeric methoxyhydrin, on the basis of its NMR spectrum alone. Due to the strong intramolecular hydrogen bond of the OH proton to the methoxy oxygen ($\Delta\nu$, IR = 103 cm^{-1}) exchange of this proton was significantly retarded[6] so that coupling with the 3-*endo*-proton could be observed. In CCl_4 solution the resonance due to the 3-*endo*- and OH protons (Fig 1) gave an AB system ($J_{3n,OH} = 7{\cdot}8$ Hz). On exchange with D_2O this collapsed to the expected narrow doublet assigned to H-3*n*. The two lines of the 3-*endo*-proton signal were further split into a pair of doublets by its coupling with H-7*a* ($J_{3n,7a} = 1{\cdot}5$ cs), a characteristic "*endo-anti*" long range interaction.[3] While strong intramolecular H-bonding should also be evidenced in VII's IR spectrum, its 3-*endo*, OH coupling in the NMR spectrum should not be as large as 7·8 Hz since coupling through four or more bonds is normally in the 0–3 Hz range.[3]



V



VI



VII

Apparently phenyl participation is not involved in the methanol epoxide ring opening process.[7] That hydroxyacetate V resulted from the acetic acid addition rather than the isomeric tertiary acetate, is probably due to intramolecular isomerization of the initially formed less stable tertiary acetate to the more stable secondary acetate (V). A similar hydroxyacetate isomerization has been reported.[8]

III also reacted with LAH to give the known alcohol, 3-*endo*-phenyl-2-*exo*-norbornanol,[9] and with phenylmagnesium bromide to give 3,3-diphenyl-2-*exo*-nor-

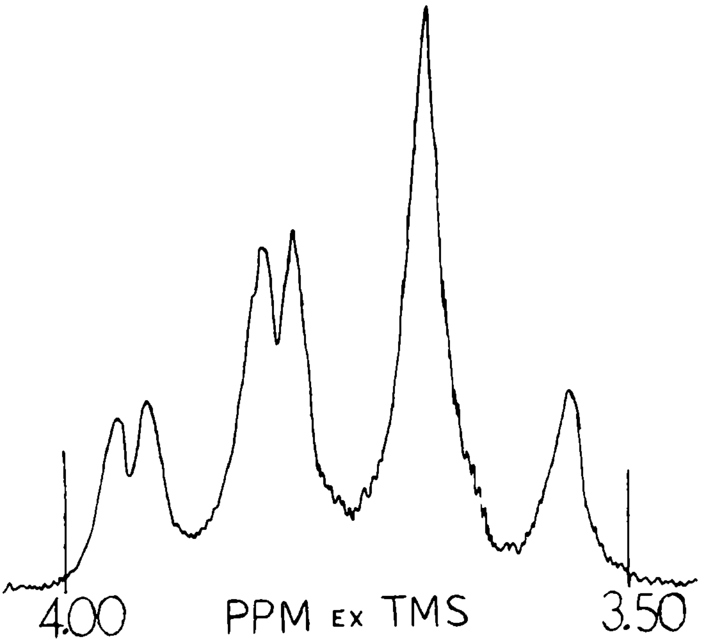
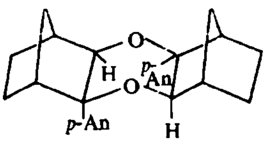


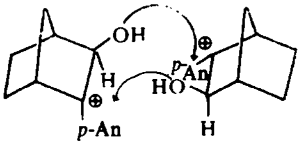
Fig 1. The 3-*endo*- and hydroxyl proton portion of the 60 MHz NMR spectrum of VI in CCl_4

bornanol.[10] The compound reported to be II failed to react with any of the reagents which reacted with III or with those known to react with norbornene-2,3-*exo*-oxide. 1-*p*-anisylcyclohexene oxide also reacted readily with methanol and acetic acid and showed no restricted rotation of the anisyl ring in its room temperature NMR spectrum.

At the outset of this investigation the acid catalyzed dehydration product of I was postulated to be the 1,4-dioxane (VIII), formed by intermolecular combination of initially formed 3-*exo*-hydroxy-2-*p*-anisylnorbornyl cations (IX). This product was initially discounted due to a Rast method molecular weight determination of less than 200,[11] and the absence of any significant peaks above *m/e* 200 in the mass spectrum. A more recent molecular weight determination by vapour pressure osmometry in $CHCl_3$ gave a value of 428[12] indicating VIII, or some stereoisomer, to be the actual reaction product. Evidently the mass spectrum showed predominantly the 2-*p*-anisylnorbornene radical cation (X) fragmentation product. Repetition of the mass spectrum of VIII on a Consolidated Electronics Corp. 21–110 mass spectrometer has shown a peak at *m/e* 432, relative intensity *ca* 0·9%. A peak at *m/e* 232 (*ca*

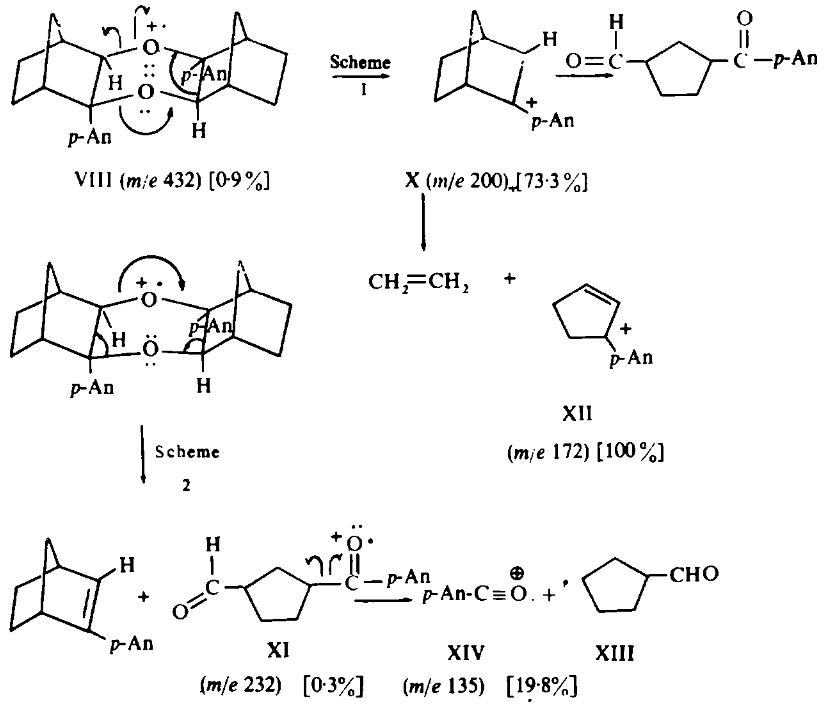


VIII



IX

0·3%) was also observed, indicating the dual fragmentation of VIII. From this dual pathway one can form both X and the radical cation XI. The former can decompose with loss of ethylene to give XII, while the latter can lose C_6H_9O, possibly as XIII, to give the *p*-anisoyl cation (XIV). These dual schemes are represented below. The mass spectrum of 1,4-dioxane[13] shows similar decomposition with the main fragment corresponding to ionized ethylene.



1-*p*-anisylcyclohexane-1,2-*cis*-diol gave only 2-*p*-anisylcyclohexanone upon treatment with 30% HCl in THF. Hydride shift affording ketone may occur directly from the initial cation in the cyclohexyl system. However, the propensity for *exo* hydrogen migration in the norbornyl system is well documented,[14] and for the required epimeric 3-*endo*-hydroxycation to form, ion IX must suffer subsequent rearrangements through two less stable secondary cations.[15] No dimer was obtained from similar treatment of the phenyl, *p*-chlorophenyl, and *p*-tolyl analogs of I. Presumably the cations analogous to IX formed from these diols are not as long-lived as IX.

Analysis of the NMR spectra of VIII *and the deuterio derivative* (VIIIa). A nearly complete analysis of the 100 MHz spectrum of VIII in $CDCl_3$ solution was undertaken. Irradiation of the δ 2·61 peak assigned to H-7*s* allowed assignment of the H-7*a* signal to δ 1·31 by a hidden-proton experiment. Irradiation of this latter signal removed the geminal coupling of 8·8 Hz from the signal at δ 2·61 and significantly narrowed the multiplet at δ 2·29 (2H's) and the δ 3·55 signal (1H). These latter signals are, therefore, assigned to the bridgehead protons and to H-3*n*, respectively. Irradiation of the δ 2·29 multiplet caused the H-3*n* signal to collapse to a doublet ($J_{3n,\,7a} = 1{\cdot}2$ Hz). The shape of the 3-*endo*-proton signal was not altered by irradiation of the δ 2·61 signal. Finally, irradiation of the signal at δ 1·31 narrowed the H-3*n* signal but no doublet separation ($J_{3n,\,4}$) could be observed.

Greater separation of the aryl hydrogen signals was observed in the 100 MHz spectrum (Fig 2) compared to the 60 MHz spectrum.[1] The spectrum was analyzed by the LAOCN3 method of Bothner-By and Castellano.[16] Data in Table 1 correspond to the final iteration (RMS error = 0·052), and the experimental spectrum has been superimposed upon the theoretical (line) spectrum in Fig 2.

TABLE 1. NMR parameters for the aromatic protons of VIII

Chemical shift (Hz at 100 MHz)	Probable error*
H(1) 641·824	0·018
H(2) 653·488	0·018
H(3) 693·490	0·015
H(4) 747·473	0·015
Coupling constants (Hz)	
J (1, 2) 8·360	0·021
J (1, 3) 0·130	0·025
J (1, 4) 2·289	0·024
J (2, 3) 2·761	0·024
J (2, 4) 0·173	0·024
J (3, 4) 8·586	0·021

* The probable error quoted is taken directly from the computer output. The actual uncertainty of the parameters is probably better represented by the experimental accuracy of the measurement of the position of the individual lines (here ± 0·05 Hz)

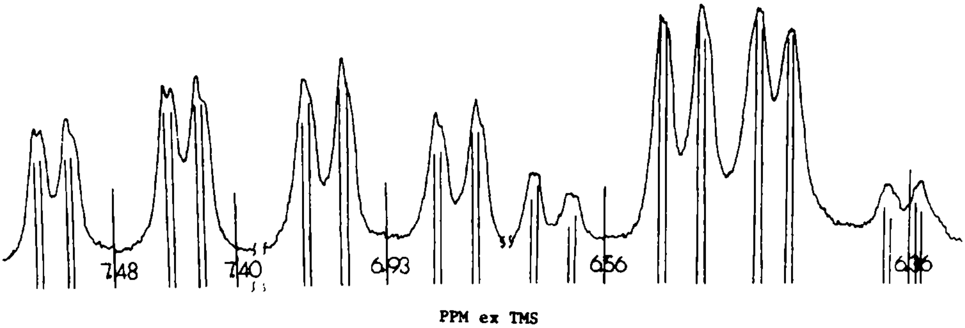
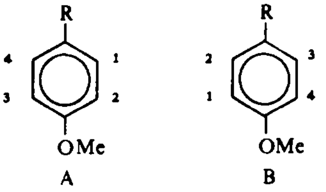


FIG 2. Aryl portion of the 100 MHz NMR spectrum of VIII in CDCl$_3$ superimposed upon the theoretical (line) spectrum

In further confirmation the irradiation of the most downfield absorption (δ 7·47) caused the small splitting (*ca* 2·1 Hz) in the most upfield absorption (δ 6·42) to collapse, thereby proving that these two hydrogens are *meta* coupled.

Given the usual ranges of magnitude of *ortho*, *meta* and *para* coupling constants[17] the data in Table 1 show conclusively that the aromatic protons are attached to a *para* disubstituted benzene. The appearance of an ABCD pattern, instead of the expected AA'BB' pattern, from a *para* substituted anisole can be explained by assuming rotation of the ring is slow on the NMR time-scale.

The parameters listed in Table I are consistent with two sets of assignments, A and B (R = norbornyl nucleus):



Assignment A was chosen on the following grounds:

(1) The *meta* coupling across the methoxyl should be larger than that across an alkyl substituent, and $J_{2,3}$ (2·76 Hz) is significantly larger than $J_{1,4}$ (2·29 Hz).

(2) The average of the chemical shifts of H_1 and H_4 is δ 6·95 while the average of H_2 and H_3 is δ 6·74. Protons *ortho* to OMe are expected to be further upfield.[18]

(3) Direct comparison of the spectra of VIII with VIIIa, the 3,5-dideuterio derivative (actually the 3,5,3',5'-tetradeuterio derivative*) in the same solvent shows that the unexchanged protons correspond to the extreme upfield and extreme downfield protons of the 4-spin system. Since the preparation of VIIIa initially involved metalation and exchange of the protons *ortho* to the OMe (Experimental), the unexchanged protons must be *meta* to the OMe, and assignment A is confirmed.

Elevated temperature NMR spectra and determination of the barrier to rotation about the sp^2–sp^3 *carbon–carbon bond.* The aryl portion of the NMR spectrum of VIII was analyzed in both diglyme and triglyme and chemical shifts were practically identical (within 1 Hz) in these two solvents at the same concentration (w/v). Collapse of the aryl portion to the anticipated AA'BB' pattern in diglyme solvent did not occur before the solvent began to boil at 160°, but greater collapse closely approaching this pattern did occur at 195° when triglyme was used as the solvent. The temperature variability of the spectra was reversible in both solvents. Portions of the spectra in both solvents at various temperature intervals are reproduced in Fig 3.

Approximate analysis of the "low temperature" spectrum for VIII in triglyme gives H_1: 6·33; H_2: 6·46; H_3: 6·83; and H_4: 7·35 δ from HMDS as internal standard, which is close to the $CDCl_3$ data (Table 1) and certainly in the same order. The assignments arrived at previously required that under conditions of fast exchange, i.e. at "high-temperature," H_1 and H_4 should average out to give the downfield part of the AA'BB' pattern and H_2 and H_3 to give the upfield part. The calculated averages are δ 6·84 and 6·64 while analysis of the "high temperature" spectrum (Fig 3) as an

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* Since all assignments in VIII and VIIIa correspond to either or both aryl rings, only one aryl ring will be referred to for the sake of simplicity.

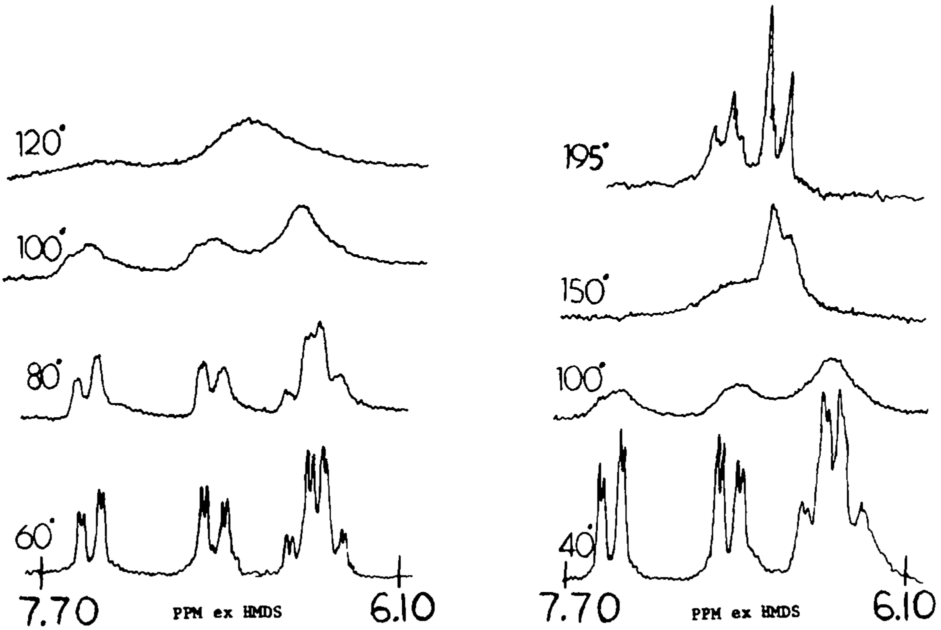
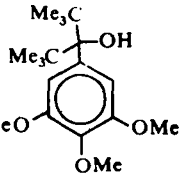


FIG 3. Aryl portion of the 100 MHz spectrum of VIII in diglyme (left) and triglyme (right) at various temperatures

approximate $(AB)_2$ gives δ 6·83 and 6·60. Any alternative assignment is very much further out.

Since the 4-spin system of VIII would give a pattern too complex for coalescence temperature analysis and determination of the free energy barrier to rotation, the 3,5-dideuterio analog (VIIIa) was chosen for this portion of the study. An excellent review of the detection of hindered rotation and inversion by NMR analysis has recently appeared.[19] The approximation of Woodbrey and Rogers[20] was employed in which the resonances for the aromatic protons are recorded at temperatures below the coalescence temperature and the values for r = Imax/Imin are measured. From these values one can obtain the rates (k) of rotation and the free energy barrier (ΔG). In the present case, the very large $\Delta\nu/J$ ratio (102·2/2·2) makes the Rogers–Woodbrey approximation particularly satisfactory. The data thus obtained are collected in Table 2.

There are several precedents[21, 22] for high energy barriers to rotation about benzylic bonds and the free energy of activation for VIIIa (Table II) is within 1 kcal/mole of the value for XV in diglyme.[21]



XV

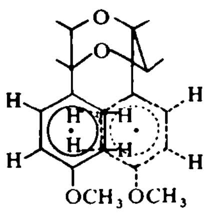
TABLE 2. ACTIVATION PARAMETERS FOR VIIIa

Corrected Temp. (°C)[a]	r	k (sec.$^{-1}$)	ΔG^{*} (kcal/mole)
113·5	4·39±0·47	79·5±4·6	19·5
117·5	3·57±0·28	88·6±3·8	19·6
120·0	2·77±0·11	101·8±2·3	19·6
122·0	2·36±0·12	111·5±3·3	19·6
124·0	2·04±0·05	121·5±1·8	19·7
126·0	1·89±0·06	127·3±2·5	19·8
128·0	1·82±0·07	130·2±3·1	19·8

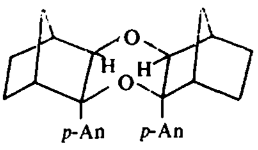
[a] The temperature was checked by immediate recalibration over the used range with ethylene glycol (Varian method) and by the "melting point method" in which samples with known melting points are placed in sealed capillaries and immersed in a liquid (here dimethylsulphoxide) in an NMR tube. The melting point is determined by the appearance of the signal of the melting sample. The two calibrations gave very similar results and the correction adopted was a compromise between them. Corrected temperatures are therefore accurate to at least ± 1 .

[b] The free energies are accurate to within ± 0·1 kcal/mole.

Further structural interpretations about VIII. The difference of 1·05 ppm for normally magnetically equivalent protons (H-1 and H-4 in Table 1) is remarkable. The chemical shift assignments for the *o*- and *m*-protons (*o*- and *m*- relative to OMe) of the diol I may be used as a model for the aryl protons of a normal, rotationally unrestricted, compound. These assignments are δ 6·88 and δ 7·38, respectively, in $CDCl_3$ solvent. Compared to these assignments the protons of VIII appear as follows, where + and − stands for shifts upfield and downfield, respectively: H_1, + 0·96; H_2, + 0·35; H_3, − 0·05; H_4, − 0·10. In view of the magnitude of the effect, it is reasonable to assume that they are due to mutual shielding by the aromatic rings. For the two protons on one side of a ring to be shielded and the two on the other side deshielded, but for the same protons on both rings to show identical chemical shifts, both rings must be symmetrically disposed. However, the upfield *o*- and *m*-protons are shielded by different amounts. Evidently the planes of the two aromatic rings are not parallel to one another but are bent away from one another, or, less likely, the methoxy substituent shifts the maximal shielding cone of the benzene ring away from its mid-point, either effect causing greater anisotropic shielding of the *meta*-protons. An end-on view of the relative positions of these aryl hydrogens is depicted below (XVI). Another structure for the dimer (XVII) in which the aryl rings are also *cis* and proximate to one another is designated as improbable on mechanistic grounds.



XVI



XVII

Note. While this work was being prepared for publication, a communication appeared elsewhere[23] confirming the dimeric nature of the acid catalyzed dehydration product of I.

EXPERIMENTAL

Unless otherwise specified, all ether and ligroine solns were dried over Na_2SO_4 prior to solvent removal. M.ps were determined in soft capillary tubes using a Mel-Temp apparatus (Laboratory Devices, Cambridge, Mass.) and are uncorrected. The IR spectrum for the O—H stretching vibration of the methoxyhydrin was obtained on a Perkin–Elmer Model 421 grating spectrometer, calibrated against polystyrene standard. All other IR spectra were recorded on a Beckman Model 5A (Only pertinent absorption frequencies are listed). UV spectra were obtained with a Cary 14 Recording Spectrophotometer. Mass spectra were obtained with a Consolidated Electronics Corp. 21–110 mass spectrometer. NMR spectra were obtained with a Varian A60 or a Varian HA100 spectrometer.

NMR data in the Experimental are given in the following manner: chemical shifts (δ) are in ppm from internal TMS. Multiplicity: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dt, doublet of triplets, etc; m, multiplet; b, broad; (exch.), exchanges on shaking with D_2O. Where the nature of the spin system is stated (e.g. AB, AA'BB') the spectrum was analyzed to the extent indicated by the data quoted. Relative intensities are given in numbers of protons, e.g. "3H" denotes a relative intensity of three protons. Coupling constants (J) are in Hz.

Whenever necessary spin–spin interactions were verified by frequency sweep decoupling. All data are considered significant to ±2 of the last significant place quoted unless otherwise stated. Unless otherwise stated, NMR data refer to 5–10% (w/v) solutions in $CDCl_3$ or CCl_4.

Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee, and by Weiler and Strauss (now Strauss only) Microanalytical Laboratory, Oxford, England.

2-*Phenylnorbornene*-2,3-exo-*oxide* (III). To a mixture of MeOH (54 ml), benzonitrile (9·0 g), $KHCO_3$ (1·5 g), and 2-phenylnorbornene[24] (15·0 g) was added 50% H_2O_2 (6·0 ml). The mixture was stirred at 10° for 48 hr, then poured into ice water, and extracted with $CHCl_3$ and ether. Evaporation of the extracting solvents gave a yellow oil to which CCl_4 was added to precipitate the by-product of benzamide. After filtration of the benzamide, the CCl_4 was evaporated from the filtrate and the residual oil was distilled *in vacuo* to give 12·6 g (76·8%) colourless oil, b.p. 100–105°/0·8 mm; UV (cyclohexane) λ_{max} 210 mμ (ε, 6590), 226 mμ (ε, 7970), 258 mμ (ε, 140); NMR and pertinent mass spectral data in text.

2-p-*Chlorophenylnorbornene*-2,3-exo-*oxide* (IV). The preparative procedure was identical to that employed for III except that the reaction time was 60 hr. Quantities used: MeOH (20 ml), benzonitrile (3·0 g), $KHCO_3$ (0·5 g), 2-*p*-chlorophenylnorbornene[24] (5·51 g), m.p. 51–52, and 50% H_2O_2 (2·0 ml). After removal of the benzamide, recrystallization of the CCl_4 evaporated filtrate with ligroine gave 2·83 g (47·4%), m.p. 44–45°; UV (cyclohexane): λ_{max} 207 (ε, 4970), 234 (ε, 10,100), 263 (860); NMR ($CDCl_3$): δ 7·30 (4H, s, Ar); 3·36 (1H, d, H-3); 2·82 (1H, m, H-1); 2·58 (1H, m, H-4); 1·8–1·1 (5H, m, H-7*s*, H-5*x*, 6*x*, 5*n*, 6*n*); 0·85 (1H, dm, H-7*a*); pertinent mass spectral data in text. (Found: C, 70·48; H, 5·83; Cl, 16·11. $C_{13}H_{13}OCl$ requires: C, 70·75; H, 5·90; Cl, 16·10%).

Attempted preparation of 2-p-*anisylnorbornene*-2,3-exo-*oxide* (II). When the Payne epoxidation procedure was employed on 2-*p*-anisylnorbornene, no epoxide was formed, even when the reaction was conducted at ice-bath temp. The NMR spectrum of the product, after benzamide removal, indicated the presence of a mixture of methoxyhydrin and unknown reaction products. Three different absorptions tentatively assigned to aryl methoxy methyls were observed at δ 3·72, 3·68, and 3·65; only one alkyl methoxy methyl absorption was observed at δ 2·85. The integral ratio of the former three absorptions relative to the latter δ 2·83 signal was *ca* 5:1. No olefinic absorption attributable to 2-*p*-anisylnorbornene was observed at δ 6·1–6·2.

2-Endo-*phenyl*-3-exo-*acetoxy*-2-*norbornanol* (V). A mixture of III (0·60 g) and AcOH (30 ml) was stirred for 6 hr at room temp. The soln was poured into ice water, extracted with ether, and the extracts were washed with Na_2CO_3 aq to neutrality. Evaporation of solvent gave 0·82 g (94%) pale yellow oil; IR(CS_2): 3600, 3500 (OH); 1740 (C=O); NMR ($CDCl_3$): δ 7·37 (5H, m, Ar); 5·14 (1H, d, $J_{3n,7a}$ = 2·0 Hz, H-3); 2·72 (1H, b, exch, OH); 2·38, 2·23 (2H, m, H-1, 4); 2·31 (1H, dm, H-7*s*); 1·98 (3H, s, Me); 1·5–0·8 (5H, m, H-7*a*, 5*x*, 6*x*, 5*n*, 6*n*). The spectrum was identical with those from the reaction of 2-phenylnorbornene with buffered peracetic acid and by the acetylation of 2-phenylnorbornane-2,3-*cis*-*exo*-diol[9] with Ac_2O in pyridine.

3-Endo-*phenyl*-3-exo-*methoxy*-2-exo-*norbornanol* (VI). A mixture of III (5·0 g) and MeOH (40 ml) was stirred for 48 hr at room temp. The soln was poured into ice water, and extracted with ether. Evaporation of the ether, followed by distillation of the residual yellow oil *in vacuo* gave 5·7 g (97%) colourless oil, b.p. 108–110°/0·6 mm; high resolution IR (CCl_4): 3516 (ν_b, $\Delta\nu = 103$ *vs* *exo*-norbornanol, 3619;[9] NMR (CCl_4): δ 7·36 (5H, m, Ar); 3·88 (1H, dd, H-3) and 3·60 (1H, d, exch., OH), see text; 2·93 (3H, s, Me); 2·81 (1H, m, H-4); 2·16 (1H, m, H-1); 2·09 (1H, dm, H-7*s*); 1·7–1·0 (5H, m, H-7*a*, 5*x*, 6*x*, 5*n*, 6*n*). The *p*-toluene-sulfonate, prepared in the usual manner,[25] recrystallized from ether to give m.p. 135–137°. (Found: C, 67·71; H, 6·43. $C_{21}H_{24}O_4S$ requires: C, 67·47; H, 6·45%).

1-p-*Anisylcyclohexane*-cis-1-*hydroxy*-2-*acetate*. To a soln of 1-*p*-anisylcyclohexene (10·0 g), m.p. 35–36° (lit.[26] m.p. 36°), and $CHCl_3$ (20 ml) was added slowly a slurry of 40% peracetic acid (12·5 ml) and NaOAc (2·5 g) with temp maintenance at 0°. After stirring for 16 hr at *ca* 10°, excess Na_2CO_3 was added, and the mixture was extracted with $CHCl_3$. Evaporation of the $CHCl_3$ gave a yellow-white solid, which gave 8·25 g (58·5%) white solid, m.p. 194–196°, after recrystallization from ligroine (b.p. 60–70°); IR (CS_2): 3570 (OH), 1740 (C=O); NMR (CCl_4): δ 7·32 (2H, *o*-Ar H's) and 6·80 (2H, *m*-Ar H's), AA'BB' system; 5·22 (1H, bt, H-2); 3·80 (3H, s, OMe); 2·1–1·5 (8H, m, ring H's); 1·80 (3H, s, Me). By analogy with the method of preparation of V, V's NMR spectrum, and that of 1-*p*-anisylcyclohexane-1,2-*cis*-diol, the acetoxy group is assumed to be at C-2. (Found: C, 67·90; H, 7·26. $C_{15}H_{17}O_4$ requires: C, 68·16; H, 7·63%).

1-p-*Anisylcyclohexane*-1,2-cis-*diol*. 1-*p*-anisylcyclohexane-*cis*-1-hydroxy-2-acetate (6·6 g) was dissolved in a soln of KOH (2·1 g), water (15 ml), and EtOH (95 ml) and the resultant soln was refluxed for 2·5 hr. Most of the EtOH was evaporated, the residue was added to water, and the light yellow solid that formed was filtered. Recrystallization from $CHCl_3$-ligroine gave 4·2 g (76%) white solid, m.p. 102–103° (lit.[27] m.p. 106–107°); NMR ($CDCl_3$): δ 7·45 (2H, *o*-Ar H's) and 6·93 (2H, *m*-Ar H's), AA'BB' system; 4·0 (1H, m, H-2); 3·83 (3H, s, Me); 2·61 (1H, exch, OH); 2·0–1·5 (8H, ring H's). (Found: C, 70·49; H, 8·23. $C_{13}H_{17}O_3$ requires: C, 70·24; H, 8·16%).

2-p-*Anisylcyclohexanone*. To a soln of 1-*p*-anisylcyclohexane-1,2-*cis*-diol (1·5 g) and THF (10 ml) was added conc HCl (5·0 ml). The resultant yellow soln was heated on a steam bath for 10 min, water (10 ml) was added, and heating was continued for an additional 15–20 min, during which time a light brown oil settled out of soln. The mixture was added to ice water, and the light yellow solid that formed was filtered. Recrystallization from ligroine gave 1·1 g (79%) of ketone, m.p. 87–88° (lit.[28] m.p. 89–90°); IR (CS_2): 1720 (C=O). (Found: C, 76·45; H, 7·74. $C_{13}H_{15}O_2$ requires C, 76·44; H, 7·90%).

1-p-*Anisylcyclohexene*-1,2-*oxide*. The preparative procedure was identical to that employed for III, except for the reaction time being 12 days, and the temp 30°. Quantities used: MeOH (40 ml), benzonitrile (4·9 g), $KHCO_3$ (1·0 g), 2-*p*-anisylcyclohexene (10·0 g), and 50% H_2O_2 (4·0 ml). After removal of the benzamide and evaporation of the CCl_4, a yellow oil was obtained whose NMR spectrum indicated it to be the epoxide contaminated with a small amount of alkene (δ 6·00, m, —C=C—H). This mixture was dissolved in ligroine, decolorized with charcoal, and the epoxide crystallized in a dry ice-acetone bath. Since the product melted at room temp, the solvent was decanted, and the process repeated to give 3·0 g, (28%) pure (NMR analysis) product; NMR($CDCl_3$): δ 7·34 (2H, *o*-Ar H's) and 6·89 (2H, *m*-Ar H's), AA'BB' system; 3·81 (3H, s, Me); 3·08 (1H, t, H-2); 2·4–1·3 (8H, m, ring H's).

Dehydration of 2-p-*anisylnorbornane*-2,3-cis-exo-*diol to the dimer* (VIII). To a soln of I (14·8 g) in THF (100 ml) was added conc HCl (50 ml) and the resultant soln was heated on a steam bath for 15 min. Then water (25 ml) was added and heating was continued for an additional 10 min. Upon cooling in an ice bath solid VIII formed and was filtered, and washed with ligroine to give 6·30 g. The ligroine was evaporated from the filtrate, more water (50 ml) was added, and the mixture was allowed to sit for 1·5 hr. The solid that formed was filtered and washed with ligroine to give 1·15 g additional material, 7·45 g (54·6%) total yield. Recrystallization from EtOH gave m.p. 193–194°; UV (95% ethanol): λ_{max} 229 mμ (ε, 11,300), 277 mμ (ε, 1550), 284 mμ (ε, 1450); NMR and pertinent mass spectral data described in text. (Found: C, 77·69; H, 7·37. $C_{28}H_{32}O_4$ requires: C, 77·75; H, 7·66%).

Preparation of the 3,5-*dideuterio analog of* VIII (VIIIa). 2,6-dideuterioanisole was prepared by the metalation of anisole with n-BuLi followed by hydrolysis with 99·5% D_2O according to the method of Shirley *et al.*[29] The hexane soln from the initial metalation was metalated again in the same manner. The dideuterio anisole was brominated by the method of Shirley[30] to give 2,6-dideuterio-4-bromoanisole (*ca* 75% pure according to NMR integral analysis; principle impurity was the monodeuterio derivative). The bromide was converted to the Grignard reagent, treated with norcamphor to give the 2-*exo*-*p*-anisylnorbornornanol, and thermally dehydrated to the alkene as described previously.[24] Subsequent reactions as reported elsewhere[31] for the undeuterated material gave the 3,5-dideuterio analog of I which, in turn, was converted to VIIIa by the method described above for VIII. While VIIIa was contaminated with less than 100% deuterium incorporation at the 3,5- (and 3',5') positions, the impurity did not seriously affect the subsequent barrier height analysis.

Attempted dehydration of other diols to form dimers (p-*dioxanes*). The diols 2-phenylnorbornane-2,3-*cis-exo*-diol,[32] the *p*-chloro-,[33] and *p*-methyl-[34] derivatives were reacted in the same manner as described for the preparation of VIII. Examination of the NMR spectra of the ether evaporated extracts showed no *p*-dioxane, as evidenced by the normal aryl proton signals; the IR spectra showed the presence of OH and CO groups suggesting chlorohydrin and ketone products. No attempts were made at further characterization.

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