

8. EPOXIDATION OF 3-ARYLOXY-4-METHYL-3,6-DIHYDRO-2H-PYRANS

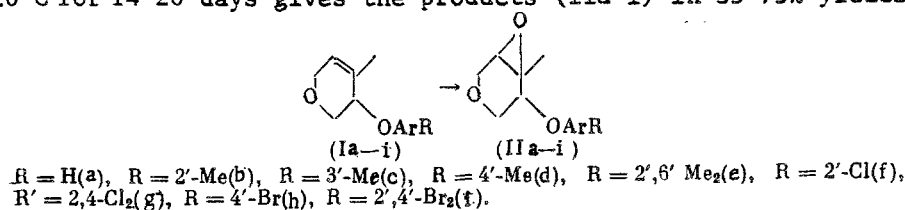
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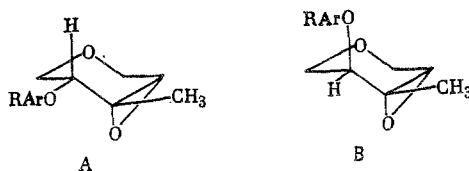
The preparation of epoxides from unsaturated cyclic ethers and peracids has received considerable attention [1-4]. It has been found that when alkyl substituents are present in the α -position to the heteroatom [2, 3], epoxidation gives *cis-trans* isomers, but when aryl substituents are present, only the *trans* isomers are formed [4].

We have now continued these studies with 3-aryloxy-4-methyl-3,6-dihydro-2H-pyrans (I), and monoperphthalic (MPPA) and peracetic (PAA) acids.

The starting ethers (Ia-i) were synthesized by known methods from 4-methyl-5,6-dihydro-2H-pyran [5], and their properties are given in Table 1. Epoxidation of (Ia-i) by treatment with MPPA at $\sim 20^\circ\text{C}$ for 14-20 days gives the products (IIa-i) in 35-75% yields:



In principle, the epoxides (II) may exist as two isomers, A (*trans*) and B (*cis*), and each of these as two conformers:



According to GLC and TLC, two compounds were obtained in all cases. They were identified by ^{13}C NMR (Table 2).

All the ring carbon atoms give two nonequivalent signals, confirming the presence of two isomers. The most important signals for the interpretation of the structures of (II) are those for C³ and C⁴. Signals of highest intensity are seen at higher field, characteristic of *cis*-oriented substituents [6], in this instance OArR and CH₃ (B). A considerable shift of the signals for the other isomer to lower field (>2 ppm) is seen only for C³, indicating the *trans*-orientation of the substituents, i.e. supporting isomer A in the conformation shown in the diagram. The ratio of the other isomers of (II) in Table 2 is based on GLC data, bearing in mind that in all known cases (II d, f, g) the *trans*-isomers have smaller retention times than the *cis*-isomers.

With PAA, the reaction with (I) is complete after 5 days at 40°C , but the *cis-trans* isomer ratio remains unchanged. It is known that the allyl alkoxy-group has a *trans*-orienting effect in the epoxidation of the corresponding dihydropyrans [7]. To judge from the results obtained here, the aryloxy-group has the same influence, but to a lesser extent. The nature of the substituent in the benzene ring has no significant effect, but screening of the oxygen atom by two neighboring CH₃ groups (Ie) substantially reduces the stereoselectivity of the reaction.

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TABLE 1. Physicochemical Properties of 3-Aryloxy-4-methyl-3,6-dihydro-2H-pyrans

Compound	R	Bp, °C (p, mm Hg), Mp, °C	n_D^{20}	Yield, %	PMR spectrum, δ , ppm			
					4-CH ₃ (3H)	CH ₃ -Ph	CH ₃ -O-CH ₃ , CH-O (5H)	aromatic
(Ia)	H	120 (2-3)	1,5495	57	1,75s	—	3,7-4,4 m	5,4 s 6,5-7,2 m(5H)
(Ib)	2'-Me	105 (2-3)	1,5458	55	1,80s	2,1s (3H)	3,5-4,3 m	5,5 s 6,5-7,0 m(4H)
(Ic)	3'-Me	90 (2-3)	1,5438	54	1,75s	2,2s (3H)	3,6-4,5 m	5,5 s 6,5-7,2 m(4H)
(Id)	4'-Me	120 (2-3)	1,5425	55	1,65s	2,2s (3H)	3,5-4,4 m	5,5 s 6,5-7,0 m(4H)
(Ie)	2',6'-Me ₂	113 (2-3)	1,5410	35	1,80s	2,2s (6H)	3,0-4,0 m	5,5 s 6,6-7,2 m(3H)
(If)	2'-Cl	154 (2-3)	1,5580	74	1,75s	—	3,7-4,5 m	5,6 s 6,6-7,3 m(4H)
(Ig)	2',4'-Cl ₂	87-89	—	70	1,80s	—	3,5-4,5 m	5,5 s 6,6-7,4 m(3H)
(Ih)	4'-Br	49-51	—	49	1,75s	—	3,7-4,5 m	5,7 s 6,7-7,5 m(4H)
(Ii)	2',4'-Br ₂	80-81	—	58	1,75s	—	3,5-4,5 m	5,6 s 6,6-7,4 m(3H)

TABLE 2. Physicochemical Properties of 3-Aryloxy-4-methyl-4,5-epoxytetrahydropyrans

Compound	R	Bp, °C (p, mm Hg), Mp, °C	n_D^{20}	Yield, %		Isomer ratio, A:B	PMR spectrum, δ , ppm
				MPPA	PAA		
(IIa)	H	116 (2-3)	1,5410	61	63	5:1	1.4 s (3H, CH ₃), 3.0 d (1H, CH-CO), 3.5-4.2 m (5H, CH ₂ -O-CH ₂ , CH-OAr), 6.5-7.2 m (5H, Ar)
(IIb)	2'-Me	130 (2-3)	1,5175	76	-	10:1	1.5 s (3H, CH ₃), 2.2 s (3H, CH ₃ Ar), 3.0 d (1H, CH-CO), 3.2-4.0 m (5H, CH ₂ -O-CH ₂ , CH-OAr), 6.6-7.4 m (4H, Ar)
(IIc)	3'-Me	127 (2-3)	1,5310	51	-	13:1	1.5 s (3H, CH ₃), 2.25 s (3H, CH ₃ Ar), 3.0 d (1H, CH-CO), 3.4-4.1 m (5H, CH ₂ -O-CH ₂ , CH-O-Ar), 6.6-7.4 m (4H, Ar)
(II d)	4'-Me	125 (2-3)	1,5350	63	-	7:1	1.45 s (3H, CH ₃), 2.3 s (3H, CH ₃ Ar), 3.0 d (1H, CH-CO), 3.5-4.4 m (5H, CH ₂ -O-CH ₂ , CH-OAr), 6.5-7.0 m (4H, Ar) ¹³ C: 64.01 d (C ²), 64.73 t (C ³), 74.18 and 75.54 d (C ⁵), 56.96 and 57.86 s (C ⁴), 58.90 and 60.97 d (C ⁶), 64.01 and 64.73 t (C ⁶)
(IIe)	2',6'-Me ₂	36-37	-	40	70	3:1	1.45 s (3H, CH ₃), 2.1 s (6H, CH ₃ Ar), 2.9 (1H, CH-CO), 3.2-4.0 m (5H, CH ₂ -O-CH ₂ , CH-OAr), 6.75-6.85 m (3H, Ar)
(II f)	2'-Cl	170 (2-3)	1,5510	49	65	10:1	1.5 s (3H, CH ₃), 3.0 d (1H, CH-CO), 3.5-4.2 m (5H, CH ₂ -O-CH ₂ , CH-OAr), 6.6-7.2 m (4H, Ar) ¹³ C: 64.08 and 65.05 t (C ²), 74.76 and 75.47 d (C ³), 57.15 and 57.85 s (C ⁴), 59.16 and 61.29 d (C ⁵), 65.96 and 67.51 t (C ⁶)
(II g)	2',4'-Cl ₂	144-146	-	77	-	7:1	1.5 s (3H, CH ₃), 3.0 d (1H, CH-CO), 3.5-4.3 m (5H, CH ₂ -O-CH ₂ , CH-OAr), 6.7-7.4 m (3H, Ar) ¹³ C: 62.72 and 63.11 t (C ²), 75.00 and 75.94 s (C ³), 56.32 and 57.06 s (C ⁴), 58.52 and 60.60 d (C ⁵), 64.24 and 64.52 t (C ⁶)
(II h)	4'-Br	155 (2-3)	1,5705	71	-	9:1	1.45 s (3H, CH ₃), 2.95 d (1H, CH-CO), 3.7-4.5 m (5H, CH ₂ -O-CH ₂ , CH-OAr), 6.7-7.4 m (4H, Ar)
(II i)	2',4'-Bu ₂	105-107	-	84	-	9:1	1.50 s (3H, CH ₃), 3.0 d (1H, CH-CO), 3.5-4.3 m (5H, CH ₂ -O-CH ₂ , CH-OAr), 6.7-7.4 m (4H, Ar)

EXPERIMENTAL

IR spectra were obtained on a UR-20 (in vaseline oil), PMR spectra on a Tesla BS-487 C, operating frequency 80 MHz (in CCl₄ or CDCl₃) relative to HMDS, and ¹³C NMR spectra on a Bruker SX-900, operating frequency 22.5 MHz, in monoresonance mode with TMS.

The starting 3-aryloxy-4-methyl-3,6-dihydro-2H-pyrans shown in Table 1 were obtained as described in [5].

3-Aryloxy-4-methyl-4,5-epoxytetrahydropyrans (IIa-i).

Method 1. To a mixture of 50 ml of dry ether and 0.2 mole of the pyran (Ia-i) was added dropwise with stirring at 0°C an ether solution of 0.22 mole of MPPA, and the mixture stirred 1 h at 20°C and kept for 14-20 days. Excess MPPA was destroyed by heating the mixture for 2 h, and the mixture was neutralized with 10% sodium carbonate solution, washed with water, and dried over magnesium sulfate. The solvent was removed, and the epoxide isolated by fractionation in vacuo or by crystallization from a suitable solvent. The physicochemical properties of (IIa-i) are given in Table 2.

Method 2. To a solution of 0.1 mole of (Ia-i) in chloroform (1:3) and 0.5 g (0.006 mole) of fused sodium acetate was added dropwise with stirring 10 g (0.125 mole) of PAA at 20°C. The mixture was stirred for 2.5 h at 40°C, cooled, the organic layer separated, washed with 10% NaOH and water to pH 7, dried over CaCl_2 , the solvent removed, and the epoxides isolated as in method 1.

CONCLUSIONS

Reaction of 3-aryloxy-4-methyl-3,6-dihydro-2H-pyrans with peracids takes place stereoselectively to give trans-3-aryloxy-4-methyl-4,5-epoxytetrahydropyrans.

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CHIRAL COMPLEX FORMERS AND AGENTS FOR TRANSPHASE TRANSFER.

COMMUNICATION 3.* SYNTHESIS OF PODANDS WITH C_2 SYMMETRY

AND 24-CROWN-8-ETHER WITH D_2 SYMMETRY DERIVED FROM

FROM 1,4;3,6-DIANHYDRO-D-MANNITOL

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1,4;3,6-Dianhydro-D-mannitol (I), which was synthesized from D-mannitol [2, 3], has been used for the synthesis of chiral crown ethers containing in the macrocycle one [4] or two residues of (I) [5]. This chiral diol with C_2 symmetry is a convenient matrix for the synthesis of acyclic analogs of crown ethers, viz., the polyether podands; thanks to cis configuration of the hydroxyl groups in the derived polyethers, it should be easier to achieve the quasicyclic side chain conformation necessary for the complexation of metal cations and organic bases. In order to study the effect of polyether chain length and terminal groups on the complex-forming properties of the podands obtained from (I), we have synthesized a number of compounds of types (II)-(VIII), of which only (II) was previously known [2].

For this purpose we have used an efficient O-alkylation of sterically hindered diol (I) by reaction with the appropriate halide or tosylate in the superbasic medium NaOH-DMSO .** Compounds (II)-(VI) are obtained directly from (I) in one step, while compounds (VII) and (VIII) are obtained via diacetal (VI) in three steps (see below). The yield of podands (II)-(VI) from (I) is 57-100%, which corresponds to 19-34% based on D-mannitol. Products of in-

*For previous communication, see [1].

**For more detail concerning this method, see [6].

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