Reaction of Some Derivatives of *cis*-1,2-Cyclohexanediol and *cis*-1,2-Cyclopentanediol with Anhydrous Hydrogen Fluoride

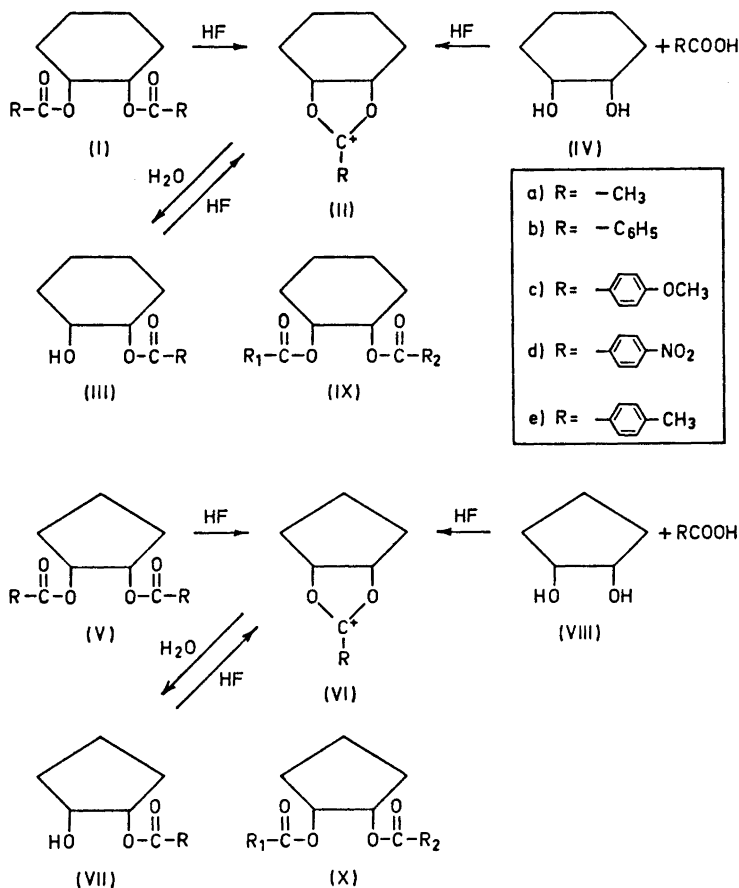INGE LUNDT and CHRISTIAN PEDERSEN

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Treatment of diacylated or monoacylated *cis*-1,2-cyclohexanediol or *cis*-1,2-cyclopentanediol with anhydrous hydrogen fluoride leads to formation of dioxolanylium ions. These ions are also formed when the unsubstituted diols are treated with a carboxylic acid in hydrogen fluoride. Subsequent hydrolysis of the dioxolanylium ions yields monoesters. The reaction of mixed diesters of *cis*-1,2-cyclohexanediol or of *cis*-1,2-cyclopentanediol with hydrogen fluoride may give two different dioxolanylium ions. It was found that mixed esters containing an acetoxy group and a *p*-nitrobenzoyloxy group gave the *p*-nitrophenyldioxolanylium ion only. When an acetoxy group was competing with a *p*-methoxybenzoyloxy group only the methyldioxolanylium ion was formed. With other mixed esters, mixtures of the two possible dioxolanylium ions were obtained.

Treatment of *cis*-1,2-diacetoxycyclohexane (Ia) with anhydrous hydrogen fluoride at room temperature leads to formation of the dioxolanylium ion (IIa) in the course of a few hours.[1] A similar treatment of *cis*-1,2-diacetoxycyclopentane (Va) yields the dioxolanylium ion (VIa) in *ca*. 30 min.[2] The corresponding *trans* compounds do not react,[1] or they react much more slowly.[2] In order to investigate this type of reaction more closely we have now studied the behaviour of a number of *cis*-1,2-cyclohexanediol and 1,2-cyclopentanediol derivatives towards hydrogen fluoride.

The reaction of diacylated *cis*-1,2-cyclohexanediols (I) and cyclopentanediols (V) with hydrogen fluoride was studied initially. The reactions were followed by NMR spectroscopy and the results are presented in Table 1. The esters were dissolved in anhydrous hydrogen fluoride at 0°C and NMR spectra were obtained after 15 – 30 min, at a stage where the esters were largely unchanged. The solutions were then kept at 0°C of at room temperature and spectra were run at intervals at 0°C. The formation of the dioxolanylium ions (IIa) and (VIa) from the two diacetates (Ia) and (Va) is easily followed since the methyl groups of these compounds give characteristic NMR signals.[1,2] The other compounds investigated contained aromatic acyl-groups which

(I)   R–C–O   O–C–R   HF →   (II)   ← HF   (IV)   HO   OH   + RCOOH

H_2O / HF

(III)   HO   O–C–R

(IX) R_1–C–O   O–C–R_2

a) R = –CH_3
b) R = –C_6H_5
c) R = –⟨⟩–OCH_3
d) R = –⟨⟩–NO_2
e) R = –⟨⟩–CH_3

(V)   R–C–O   O–C–R   HF →   (VI)   ← HF   (VIII)   HO   OH   + RCOOH

H_2O / HF

(VII)   HO   O–C–R

(X) R_1–C–O   O–C–R_2

give complicated NMR signals. The formation of dioxolanylium ions from these compounds was followed through the signals of H-1 and H-2 of the cyclohexane and cyclopentane rings. These signals in most cases occur at lower field in the ions (II) and (VI) than in the esters (I) and (V) (Table 1). As noticed by Paulsen et al.[2] the cyclopentane derivatives react more rapidly with hydrogen fluoride than the cyclohexane derivatives. The aromatic esters react more slowly than the acetates (Table 1). The di-p-nitrobenzoates (Id) and (Vd) do not form dioxolanylium ions at all in hydrogen fluoride; the solutions of these compounds turned dark in a few days and the NMR spectra indicated that decomposition took place. Hydrogen fluoride solutions of the ions (II) or (VI) are stable at room temperature for several days.

The monoesters (III) and (VII) were found to react readily with hydrogen fluoride to give the ions (II) and (VI), respectively. These reactions are easily studied by NMR spectroscopy since the spectra of the monoesters in hydrogen fluoride are quite different from the spectra of the ions which they form (Table 1). The two monoacetates (IIIa) and (VIIa) were converted into the

Table 1. Reaction of mono- and di-esters of *cis*-1,2-cyclohexanediol and cyclopentanediol with hydrogen fluoride.

Compound	Starting materials Final products		H_1, H_2	Chemical shifts in HF at 0°C Other groups	Time and temp. required for completion of reactions	Product in HF
Ia[7]	10 min,	0°C	5.5	— OAc 2.45	6 – 7 h, 22°C	IIa
	6 h,	22°C	5.7	$H_3C - {}^+C$ 2.75; HOAc 2.55		
Ib[7]	25 min,	0°C	5.7		ca. 24 h, 22°C	IIb
	24 h,	22°C	5.9			
Ic	30 min,	0°C	5.8	— OCH₃ 4.1	ca. 24 h, 22°C	IIc
	22 h,	22°C	5.8	— OCH₃ 4.1		
Id					No reaction	
Ie	30 min,	0°C	5.8	— CH₃ 2.45	ca. 24 h, 22°C	IIe
	24 h,	22°C	5.9	— CH₃ 2.48, 2.52		
Va[12]	15 min,	0°C	5.6	— OAc 2.46	1 h, 0°C	VIa
	24 h,	22°C	6.1	$H_3C - {}^+C$ 2.70; HOAc 2.55		
Vb[12]	15 min,	0°C	5.9		20 h, 0°C	VIb
	20 h,	0°C	6.2			
Vc	20 min,	0°C	5.9	— OCH₃ 4.1	4 h, 0°C	VIc
	24 h,	22°C	6.2	— OCH₃ 4.1		
Vd[13]					No reaction	
IIIa					30 min, 0°C	IIa
	30 min,	0°C	5.7	$H_3C - {}^+C$ 2.75		
IIIb	10 min,	0°C	4.5; 5.6		5 – 6 h, 0°C	IIb
	5 h,	0°C	5.9			
IIIc	10 min,	0°C	4.5; 5.7	— OCH₃ 4.1	4 h, 22°C	IIc
	4 h,	22°C	5.8	— OCH₃ 4.1		
IIId	15 min,	0°C	4.6; 5.6		1 h, 0°C	IId
	1 h,	0°C	6.1			
IIIe	10 min,	0°C	4.5; 5.7	— CH₃ 2.48	6 h, 22°C	IIe
	6 h,	22°C	5.9	— CH₃ 2.52		
VIIa					< 15 min, 0°C	VIa
	15 min,	0°C	6.1	$H_3C - {}^+C$ 2.70		
VIIb					< 30 min, 0°C	VIb
	30 min,	0°C	6.3			
VIIc					< 30 min, 0°C	VIc
	30 min,	0°C	6.2	— OCH₃ 4.1		
VIId					< 20 min, 0°C	VId
	20 min,	0°C	6.35			

corresponding ions, (IIa) and (VIa), very rapidly when dissolved in hydrogen fluoride at 0°C. The monoesters containing aromatic acyl groups reacted slower than the acetates but faster than the diesters. It may be noted that the mono-p-nitrobenzoates (IIId) and (VIId) were converted into the dioxolanylium ions (IId) and (VId), respectively, in the course of $ca.$ 1 h at 0°C whereas the di-p-nitrobenzoates did not react with hydrogen fluoride.

In connection with other work it was observed that methanol reacts with carboxylic acids in anhydrous hydrogen fluoride to give methyl esters. Thus methanol and acetic acid react almost instantaneously, when dissolved in hydrogen fluoride at 0°C, to give a quantitative yield of methyl acetate as seen from NMR spectra of the hydrogen fluoride solution. The corresponding reaction with benzoic acid is somewhat slower. On the basis of this observation, mixtures of cyclohexanediol (IV), or cyclopentanediol (VIII), with 1.2 − 2 molar equiv. of carboxylic acid were dissolved in hydrogen fluoride. NMR spectra of these solutions showed that the corresponding dioxolanylium ions, (II) and (VI), were formed in quantitative yield. Acetic acid reacted rapidly whereas the aromatic acids required longer time before the conversion to (II) or (VI) was complete (Table 2). p-Nitrobenzoic acid did not react

Table 2. Reaction of cis-1,2-cyclohexanediol and cis-1,2-cyclopentanediol with carboxylic acids in hydrogen fluoride.

Compound	Time and temp. required for complete reaction	Product in HF	Product obtained after hydrolysis
IV + 1.5 equiv. HOAc	3 h, 0°C	IIa	IIIa 75 % isolated
IV + 1.5 equiv. HOBz	10 h, 22°C	IIb	IIIb 85 % isolated
IV + 1.5 equiv. HOBzOCH₃	12 h, 22°C	IIc	IIIc 74 % isolated
IV + 1.5 equiv. HOBzNO₂	No reaction (decomp.)		
IV + 1.5 equiv. HOBzCH₃	12 h, 22°C	IIe	IIIe 90 % isolated
VIII + 1.5 equiv. HOAc	< 10 min, 0°C	VIa	VIIa 63 % isolated
VIII + 1.5 equiv. HOBz	9 h, 0°C	VIb	VIIb 39 % isolated

with (IV). When the hydrogen fluoride solutions, containing the ions (II) or (VI), were hydrolyzed, the monoesters (III) and (VII), respectively, were obtained in good yields. Thus treatment of cis-1,2-cyclohexanediol (IV) with 1.2 equiv. of benzoic acid in hydrogen fluoride gave an 85 % yield of the

monobenzoate (IIIb) Similar results were obtained with other acids (Table 2) and this reaction probably provides the most convenient method for the preparation of the monoesters (III) and (VII), uncontaminated by diesters.

The reaction of the diols (IV) and (VIII) with carboxylic acids in hydrogen fluoride probably gives monoesters as the initial products. The latter are then subsequently transformed into the stable ions (II) or (VI), as shown above. When cyclohexanol was treated with acetic or benzoic acid in hydrogen fluoride, small amounts of cyclohexyl esters were formed initially, as seen from the NMR spectra. However, in the course of 24 h these esters decomposed with formation of polymeric material.

It was found previously [3] that tetra-O-benzoyl-D-arabinopyranose and 1,3-di-O-acetyl-2,4-di-O-benzoyl-D-arabinopyranose underwent completely different reactions when treated with hydrogen fluoride. It was therefore of interest to study the behaviour of mixed esters of the type (IX) or (X) towards hydrogen fluoride.

The acetate-p-nitrobenzoates, (IXa, d) and (Xa, d), gave the p-nitrophenyldioxolanylium ions (IId) and (VId), respectively, as the sole products on reaction with anhydrous hydrogen fluoride. The acetoxonium ions (IIa) or (VIa) were not formed at all as seen from the NMR spectra of the hydrogen fluoride solutions.

The benzoate-p-nitrobenzoate (IXb, d) also gave the nitrophenyldioxolanylium ion (IId) as the only product when treated with hydrogen fluoride. In this case it was not possible to decide with certainty from the NMR spectra whether (IIb) or (IId) was formed. However, hydrolysis of the hydrogen

Table 3. Reaction of mixed esters of cis-1,2-cyclohexanediol and cis-1,2-cyclopentanediol with hydrogen fluoride.

Compound	Time and temp. required for complete reaction	Product in HF	Product obtained after hydrolysis
IX a, d	5 h, 22°C	IId	
IX a, c	3 h, 22°C	IIa	
IX b, d	ca. 24 h, 22°C	IId	IIId, isolated 77 %
IX a, b	5 h, 22°C	IIa and IIb (1 : 1)	
IX b, c	ca. 24 h, 22°C		IIIb and IIIc (2 : 1)
IX b, e	ca. 20 h, 22°C		IIIb and IIIe (2 : 1)
IX c, e	ca. 20 h, 22°C	IIc and IIe (1 : 1)	
Xa, d	2.5 h, 0°C	VId	
Xa, c	3 h, 0°C	VIa and VIc (2 : 3)	
Xa, b	2.5 h, 0°C	VIb and VIa (15 : 1)	

fluoride solution gave a 77 % yield of the mono-p-nitrobenzoate (IIId); the monobenzoate (IIIb) was not found.

When, on the other hand, the acetate-p-methoxybenzoate (IXa, c) was dissolved in hydrogen fluoride only the acetoxonium ion (IIa) was formed.

With other mixed esters a mixture of the two possible dioxolanylium ions was usually obtained (Table 3), and in view of the result obtained with (IXa,c) it may be noted, that the corresponding cyclopentane derivative (Xa,c) gave a mixture of acetoxonium ion (VIa) and p-methoxylbenzoxonium ion (VIc) in a 2 : 3 ratio.

Treatment of the acetate-benzoate (IXa,b) with hydrogen fluoride gave equal amounts of acetoxonium ion (IIa) and benzoxonium ion (IIb). Again the corresponding cyclopentane derivative (Xa,b) behaved differently, giving almost exclusively the benzoxonium ion (VIb) (Table 3).

When acetic acid was added to a solution of the benzoxonium ion (IIb) in hydrogen fluoride no reaction took place in the course of several days at room temperature; no acetoxonium ion was formed. Neither did addition of benzoic acid to the acetoxonium ion (IIa) in hydrogen fluoride lead to formation of (IIb). Hence it must be concluded that dioxolanylium ions are formed in a kinetically controlled reaction.

When, on the other hand, a mixture of the dibenzoate (Ib) and acetic acid was dissolved in hydrogen fluoride, rather large amounts of the acetoxonium ion (IIa) was formed in addition to (IIb). Since (IIb) does not react with acetic acid this result can only be explained by exchange of the benzoyl-groups of (Ib) with acetic acid to give the acetate-benzoate (IXa,b) or the diacetate (Ia). The latter two would then in turn yield the acetoxonium ion. A similar exchange reaction has been observed with carbohydrate derivatives.[4] A mixture of the diacetate (Ia) and benzoic acid gave only rather small amounts of benzoxonium ion when treated with hydrogen fluoride. Thus the reverse exchange reaction is slower, probably because Ia reacts faster with hydrogen fluoride than (Ib).

Treatment of (IXa,b) with hydrogen fluoride could yield benzoxonium or acetoxium ions. If the benzoxonium ion (IIb) is formed acetic acid is also liberated and this could exchange with unreacted (IXa,b) to give the diacetate (Ia). The latter would of course yield (IIa) on further reaction with hydrogen fluoride. Similar complications may arise when other mixed esters are treated with hydrogen fluoride, and only those esters which give one dioxolanylium ion exclusively can give clear information about the relative ease of formation of dioxolanylium ions.

From the results described above it is clear that the p-nitrobenzoxonium ion is formed more readily than the acetoxonium or benzoxonium ions. The difference between the cyclohexane derivative (IXa,b) and the cyclopentane derivative (Xa,b) is probably due to the fact that (Xa,b) reacts more rapidly with hydrogen fluoride (Table 3) and therefore allows less time for ester exchange. If this is correct it may be concluded that the benzoxonium ion is formed more easily than the acetoxonium ion. The results obtained from the mixed esters (IXb,c), (IXb,e), and (IXc,e) indicate a preference for the formation of benzoxonium ions over that of the p-methoxy- or p-methylsubstituted ions, the latter two being equal.

The mechanism proposed by Angyal *et al.*[5] for the acid catalyzed formation of dioxolanylium ions from *cis*-1,2-diacyloxy compounds may explain the results described above. In the ring-closing step of this mechanism an acylium ion is cleaved off; an electron donating substituent would stabilize this acylium ion and favour its formation. Hence, the dioxolanylium ion with the least electron donating substituent would be formed preferentially.

Since the formation of dioxolanylium ions from mixed esters takes place *via* kinetically controlled reactions the experiments described above give no information about the relative stability of these ions. Experiments that may determine this stability will be described in a forthcoming paper.

EXPERIMENTAL

Melting points are uncorrected. Thin layer chromatography (TLC) was performed on silica gel PF_{254} (Merck). For preparative TLC 1 mm thick layers on 20 × 40 cm plates were used. NMR spectra were obtained on Varian A-60 and HA-100 instruments. The structures and purity of all the compounds described below were confirmed by NMR spectra obtained in deuteriochloroform solution. NMR spectra in anhydrous hydrogen fluoride were measured in Teflon sample tubes. Positions of signals in hydrogen fluoride are given in ppm relative to internal $(CH_3)_3SiCH_2CH_2CH_2SO_3Na$.

cis-1,2-Cyclohexanediol was obtained *via* the isopropylidene derivative [6,7] from a mixture of *cis*- and *trans*-1,2-cyclohexanediol (kindly supplied by Robinson Brothers Ltd., England).

cis-1,2-Cyclopentanediol was prepared according to Owen and Smith.[8]

Mono- and di-(p-methoxybenzoyl)-cis-1,2-cyclohexanediol. To a solution of (IV) (3.0 g) in pyridine (18 ml) was added *p*-methoxybenzoyl chloride (4.41 g) in pyridine (18 ml). The mixture was kept overnight at room temperature. Water was then added, followed by methylene chloride and the organic layer was washed with 3 N sulfuric acid, aqueous sodium hydrogen carbonate, and water. Evaporation of the solvent gave 5.5 g of crude product, which was crystallized and recrystallized from ether-pentane to give 3.3 g (51 %) of mono-*p*-methoxybenzoyl-*cis*-1,2-cyclohexanediol (IIIc), m.p. 72 − 73°C. (Found: C 66.90; H 7.30. Calc. for $C_{14}H_{18}O_4$: C 67.19; H 7.25.) The material in the mother liquors was purified by chromatography on a column of silica gel giving 1.2 g (12 %) of *cis*-1,2-di-(*p*-methoxybenzoyloxy)-cyclohexane (Ic) as a syrup. (Found: C 69.06; H 6.41. Calc. for $C_{22}H_{24}O_6$: C 68.74; H 6.30.)

Mono- and di-(p-nitrobenzoyl)-cis-1,2-cyclohexanediol. *cis*-1,2-Cyclohexanediol (IV) (3.0 g) was dissolved in pyridine (10 ml) and a solution of *p*-nitrobenzoyl chloride (4.77 g, 1.0 equiv.) in pyridine (25 ml) and methylene chloride (15 ml) was added with ice-cooling. Work up as above gave 5.8 g of crude product. Two recrystallizations from ethanol yielded 950 mg of *cis*-1,2-di-(*p*-nitrobenzoyloxy)-cyclohexane (Id), m.p. 147 − 148°C.[9] The mother liquors were evaporated and the residue was crystallized from ether − pentane yielding 3.5 g (53 %) of mono-*p*-nitrobenzoyl-*cis*-1,2-cyclohexanediol (IIId), m.p. 76 − 78°C. One additional recrystallization gave the pure product, m.p. 78 − 80°C. (Found: C 58.19; H 5.79; N 5.31. Calc. for $C_{13}H_{15}NO_5$: C 58.86; H 5.70; N 5.28.)

cis-1,2-Di-(p-toluyloxy)-cyclohexane (Ie) was obtained by treatment of (IV) with 2.2 equiv. of *p*-toluyl chloride in pyridine as described above. Crystallization from hexane gave the pure product, m.p. 57 − 59°C. (Found: C 74.94; H 6.70. Calc. for $C_{22}H_{24}O_4$: C 74.99; H 6.87.)

cis-1,2-Di-(p-methoxybenzoyloxy)-cyclopentane (Vc) was obtained analogously in 80 % yield from (VIII). The product was recrystallized from ethanol, m.p. 76 − 78°C. (Found: C 67.90; H 5.88. Calc. for $C_{21}H_{22}O_6$: C 68.10; H 5.99.)

Mono-p-methoxybenzoyl-cis-1,2-cyclopentanediol (VIIc) was prepared by treatment of (VIII) with 1.0 equiv. of *p*-methoxybenzoyl chloride in pyridine. Two recrystallizations from ether − pentane gave 50 % of the pure product, m.p. 91 − 92°C. (Found: C 66.18; H 6.71. Calc. for $C_{13}H_{16}O_4$: C 66.10; H 6.84.)

Mono-p-nitrobenzoyl-cis-1,2-cyclopentanediol (VIId) was prepared in the same way.

The product was purified by preparative TLC, using ether−pentane (1 : 1) as eluent, and then recrystallized from ether−pentane. Yield 48 %, m.p. 87 − 88°C. (Found: C 57.34; H 5.30; N 5.78. Calc. for $C_{13}H_{13}NO_3$: C 57.38; H 5.21; N 5.58.)

cis-*1-Acetoxy-2-benzoyloxycyclohexane* (IXa,b). The monobenzoate (IIIb), prepared as described below, was acetylated with acetic anhydride in pyridine. Preparative TLC (ether−pentane 1 : 2) gave a pure sample as a syrup. (Found: C 68.20; H 6.83. Calc. for $C_{15}H_{18}O_4$: C 68.69; H 6.91.)

cis-*Acetoxy-2-(p-methoxybenzoyloxy)-cyclohexane* (IXa, c) was prepared by acetylation of (IIIc). Preparative TLC (ether−pentane 1 : 2) gave the pure product as a syrup. (Found: C 65.77; H 6.93. Calc. for $C_{16}H_{20}O_4$: C 65.75; H 6.89.)

cis-*1-Benzoyloxy-2-(p-methoxybenzoyloxy)-cyclohexane* (IXb, c) was obtained by benzoylation of (IIIc) as a syrup which was purified by preparative TLC (ether−pentane 1 : 2). (Found: C 71.07; H 6.13. Calc. for $C_{21}H_{22}O_5$: C 71.17; H 6.26.)

cis-*1-Acetoxy-2-(p-nitrobenzoyloxy)-cyclohexane* (IXa, d) was prepared by acetylation of (IIId), or by nitrobenzoylation of (IIIa). It was purified by recrystallization from ethanol, m.p. 104 − 105°C. (Found: C 58.74; H 5.65; N 4.51. Calc. for $C_{15}H_{17}NO_6$: C 58.64; H 5.58; N 4.56.)

cis-*1-Benzoyloxy-2-(p-nitrobenzoyloxy)-cyclohexane* (IXb, d) was prepared by benzoylation of (IIId). It was recrystallized from ethanol, m.p. 104 − 105°C (reported m.p. 82°C [10]). (Found: C 65.18; H 5.14; N 3.95. Calc. for $C_{20}H_{19}NO_6$: C 65.03; H 5.18; N 3.79.)

cis-*1-Benzoyloxy-2-(p-toluyloxy)-cyclohexane* (IXb, e) was obtained by benzoylation of (IIIe). The product was a syrup which was purified by preparative TLC (ether−pentane 1 : 2). (Found: C 74.69; H 6.41. Calc. for $C_{21}H_{22}O_4$: C 74.24; H 6.55.)

cis-*1-(p-Methoxybenzoyloxy)-2-(p-toluyloxy)-cyclohexane* (IXc, e) was prepared by treatment of (IIIe) with *p*-methoxybenzoyl chloride in pyridine. Preparative TLC (ether−pentane 1 : 3) gave the pure product as a syrup. (Found: C 71.52; H 6.39. Calc. for $C_{22}H_{24}O_5$: C 71.73; H 6.56.)

cis-*1-Acetoxy-2-(p-methoxybenzoyloxy)-cyclopentane* (Xa, c) was prepared by acetylation of (VIIc) as a syrup which was purified by preparative TLC (ether−pentane 1 : 2). (Found: C 64.58; H 6.53. Calc. for $C_{15}H_{18}O_5$: C 64.74; H 6.52.)

Preparation of monoesters with hydrogen fluoride

cis-*1-Acetoxy-2-hydroxycyclohexane* (IIIa). A mixture of cis-1,2-cyclohexanediol (1.0 g) and acetic acid (0.90 ml, 2 equiv.) was cooled in ice in a polyethylene bottle while anhydrous hydrogen fluoride (6 ml) was added. The solution was kept for 24 h at room temperature. Methylene chloride (20 ml) was then added and the mixture was poured on ice. The organic layer was washed with aqueous sodium hydrogen carbonate, dried, and evaporated leaving 1.02 g (75 %) of (IIIa).[11] An NMR spectrum showed that the product was virtually pure.

cis-*1-Benzoyloxy-2-hydroxycyclohexane* (IIIb). A mixture of (IV) (500 mg) and benzoic acid (635 mg, 1.2 equiv.) in hydrogen fluoride (5 ml) was kept overnight at room temperature. Work up gave 814 mg (85 %) of (IIIb),[10] which was pure, as seen from an NMR spectrum.

cis-*1-Hydroxy-2-(p-Methoxybenzoyloxy)-cyclohexane* (IIIc) was obtained in the same manner from (IV) (500 mg) and *p*-methoxybenzoic acid (1.0 g). The crude product (988 mg) was crystallized from ether−pentane yielding 800 mg (74 %) of (IIIc), m.p. 67 − 69°C.

cis-*1-Hydroxy-2-(p-toluyloxy)-cyclohexane* (IIIe). A mixture of (IV) (1.0 g) and *p*-toluic acid (2.0 g, 1.7 equiv.) in hydrogen fluoride (8 ml) gave 1.83 g (90 %) of virtually pure (IIIe), as seen from an NMR spectrum. A sample was purified by preparative TLC (ether−pentane 1 : 2) and obtained as a syrup. (Found: C 71.59; H 7.57. Calc. for $C_{14}H_{18}O_3$: C 71.76; H 7.74.)

cis-*1-Acetoxy-2-hydroxycyclopentane* (VIIIa) [8] was prepared as described above from (VIII) and 2 equiv. of acetic acid in hydrogen fluoride, yield 63 %. *p*-Nitrobenzoylation gave the known [8] cis-1-acetoxy-2-(*p*-nitrobenzoyloxy)-cyclopentane (Xa, d), m.p. 96 − 99°C.

cis-*1-Benzoyloxy-2-hydroxycyclopentane* (VIIIb) was prepared in the same manner

from (VII) and benzoic acid, yield 39 %. The product was a syrup which was purified by preparative TLC (ether − pentane 1 : 2). (Found: C 67.60; H 6.56. Calc. for $C_{14}H_{16}O_4$: C 67.72; H 6.50.)

Reaction of mixed esters with hydrogen fluoride

cis-*1-Benzoyloxy-2-*(p-*nitrobenzoyloxy*)*-cyclohexane* (IXb, d) (300 mg) was dissolved in hydrogen fluoride (2 ml) and the solution was kept at room temperature for 3 days. It was then worked up as described above and the product was recrystallized from ether − pentane. This gave 173 mg (77 %) of the mono-nitrobenzoate (IIId), m.p. 77 − 79°C. No other products could be detected.

cis-*1-Benzoyloxy-2-*(p-*methoxybenzoyloxy*)*-cyclohexane* (IXb, c). Treatment of this compound with hydrogen fluoride gave a crude product which was shown by NMR spectroscopy to consist of 2 parts of the mono-benzoate (IIIb) and 1 part of the mono-methoxybenzoate (IIIc). The two compounds were separated by preparative TLC (ether − pentane 1 : 1) and were found to be identical with those described above. No other products were found.

cis-*1-Benzoyloxy-2-*(p-*toluyloxy*)*-cyclohexane* (IXb, d) by the same procedure gave 2 parts of the mono-benzoate (IIIb) and 1 part of the mono-toluate (IIId).

Microanalyses were carried out by Dr. A. Bernhardt.

REFERENCES

1. Pedersen, C. *Tetrahedron Letters* **1967** 511.
2. Paulsen, H., Behre, H. and Herold, C.-P. *Fortschr. chem. Forsch.* **14** (1970) 479.
3. Pedersen, C. *Acta Chem. Scand.* **22** (1968) 1888.
4. Gregersen, N. and Pedersen, C. *Acta Chem. Scand.* **22** (1968) 1307.
5. Angyal, S. J., Gorin, P. A. J. and Pitman, M. E. *J. Chem. Soc.* **1965** 1807.
6. Christian, W. R., Gogek, C. J. and Purves, C. B. *Can. J. Chem.* **29** (1951) 911.
7. Rothstein, B. *Ann. Chim. (Paris)* **14** (1930) 461.
8. Owen, L. N. and Smith, P. N. *J. Chem. Soc.* **1952** 4026.
9. Elliott, T. H. *J. Chem. Soc.* **1958** 3752.
10. Wilson, N. A. B. and Read, J. *J. Chem. Soc.* **1935** 1269.
11. Winstein, S. and Buckles, R. E. *J. Am. Chem. Soc.* **65** (1943) 613.
12. Verkade, P. E., Coops, Jr., J., Verkade-Sandbergen, A. and Maan, C. J. *Ann.* **477** (1930) 279.
13. VanLoon, C. *Chem. Abstr.* **17** (1923) 1956.