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Investigation of the Stability of Dioxolanylium Ions Derived from 1,5-Anhydro-D-arabinitol

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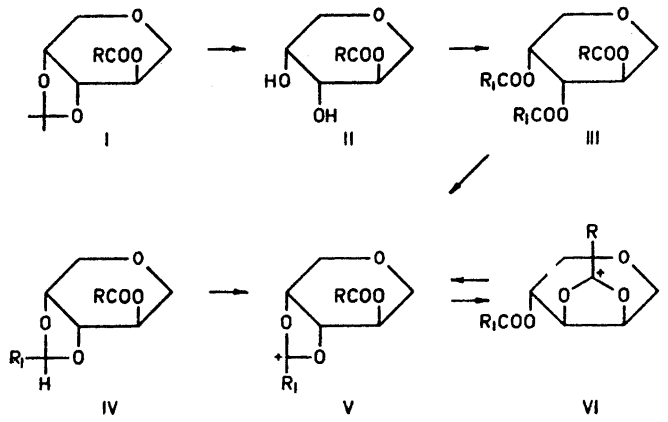
The relative stabilities of a series of dioxolanylium ions, (V) and (VI), derived from 1,5-anhydro-D-arabinitol, have been measured in hydrogen fluoride solution and in deuterioacetonitrile. The ions (V) and (VI) were prepared by treatment of triacylated 1,5-anhydro-D-arabinitol (III) with anhydrous hydrogen fluoride, or by reaction of 2-*O*-acyl-1,5-anhydro-3,4-*O*-benzylidene-D-arabinitol (IV) with triphenylmethyl fluoroborate in deuterioacetonitrile.

Reaction of *cis*-1,2-diacyloxy-cyclohexanes or cyclopentanes with anhydrous hydrogen fluoride leads to formation of dioxolanylium ions. If two different acyl groups are present two dioxolanylium ions may be formed. It was found that the less stable ion was formed as the main product in a kinetically controlled reaction.[1]

It was of interest to obtain information about the relative stability of variously substituted dioxolanylium ions, and for this purpose the equilibrium



between the isomeric ions (V) and (VI), derived from 1,5-anhydro-D-arabinitol, has been studied. These ions were prepared, either by reaction of the triesters (III) with anhydrous hydrogen fluoride, or by treatment of the benzylidene derivatives (IV) with triphenylmethyl fluoroborate.

Tri-*O*-acetyl-1,5-anhydro-D-arabinitol (III, $R=R_1=CH_3$) contains a pair of *cis*-oriented 1,2-diacyloxy groups and it would therefore be expected to give an acetoxonium ion by treatment with anhydrous hydrogen fluoride.[1-3] It was found that when the triacetate (III) was kept in hydrogen fluoride for *ca.* 5 h at 0°C a quantitative conversion to the acetoxonium ion (V, $R=R_1=CH_3$) took place. This was seen from the NMR spectrum of the hydrogen fluoride solution which showed the presence of one acetoxy group, one equivalent of acetic acid, and one signal at 2.90 ppm corresponding to an acetoxonium ion (Table 1). A similar treatment of the tribenzoate (III, $R=R_1=C_6H_5$) gave the benzoxonium ion (V, $R=R_1=C_6H_5$) in the course of 20 h at room temperature (Table 1).

Paulsen *et al.*[4,5] have investigated similar esters in the cyclohexane and cyclopentane series and on the basis of their results a rapid equilibration would be expected to take place between the ions (V) and (VI). When the triacetate or the tribenzoate (III) are the starting material (V) and (VI) are identical.[3] However, if R is different from R_1 the ions (V) and (VI) are different and the equilibrium between them should give information about their relative stabilities. To obtain this information a number of compounds (III), in which R and R_1 are different, have been prepared and their reactions with hydrogen fluoride have been studied.

When 3,4-di-*O*-acetyl-2-*O*-benzoyl-1,5-anhydro-D-arabinitol (III, $R=C_6H_5$, $R_1=CH_3$) was kept for *ca.* 20 h in anhydrous hydrogen fluoride NMR spectra showed that one equivalent of acetic acid was cleaved off and *ca.* one acetoxy-group was present (Table 1). Besides, a small amount of acetoxonium ion was formed as seen from a signal at 2.90 ppm. This shows that (III, $R=C_6H_5$, $R_1=CH_3$) is converted almost completely into the benzoxonium ion (VI, $R=C_6H_5$, $R_1=CH_3$) by treatment with hydrogen fluoride. The reaction must proceed *via* the acetoxonium ion (V, $R=C_6H_5$, $R_1=CH_3$) which rearranges to (VI) because the latter is the more stable of the two. The small acetoxonium ion signal may arise from a small amount of (V) in equilibrium with (VI). It may, however, also be due to the presence of a small amount of the acetoxonium ion (V, $R=R_1=CH_3$) which could be formed by exchange of the benzoyloxy-group of (III, $R=C_6H_5$, $R_1=CH_3$) with acetic acid, liberated in the first step. This would give (III, $R=R_1=CH_3$) which, in turn, would yield (V, $R=R_1=CH_3$). Exchange reactions of this type were found in the cyclohexane and cyclopentane series[1] and they can also take place in the present type of compounds (see below).

When the diacetate-*p*-methoxybenzoate (III, $R=p$-$MeOC_6H_4$, $R_1=CH_3$) was treated with hydrogen fluoride the product formed almost exclusively was the *p*-methoxy-benzoxonium ion (VI, $R=p$-$MeOC_6H_4$, $R_1=CH_3$). The diacetate-*p*-nitrobenzoate (III, $R=p$-$NO_2C_6H_4$, $R_1=CH_3$), on the other hand, gave the acetoxonium ion (V, $R=p$-$NO_2C_6H_4$, $R_1=CH_3$) as the sole product as seen from the acetoxonium ion signal at 2.90 ppm (Table 1).

Table 1. NMR spectra of dioxolanylium ions (V) and (VI) in anhydrous hydrogen fluoride at 0°C or in deuterioacetonitrile at room temperature. Position of signals are given in ppm relative to $(CH_3)_3SiCH_2CH_2CH_2SO_3Na$ in hydrogen fluoride and relative to tetramethylsilane in acetonitrile. When a mixture of (V) and (VI) is formed only the spectrum of the major product is given.

Product	Solvent	R	R_1	δ-Values [a]								Coupling constants							
				H_1	$H_{1'}$	H_2	H_3	H_4	H_5	$H_{5'}$	CH_3	$J_{11'}$	J_{12}	$J_{1'2}$	J_{23}	J_{34}	J_{45}	$J_{45'}$	$J_{55'}$	J_{15}
V=VI	HF	CH_3	CH_3	4.7	4.28	~6.0		5.6	4.5	3.9	2.3, 2.6 2.9	15	~0.5	~0.5		2.5	6.5	6.5	13	
V=VI	HF	C_6H_5	C_6H_5			~6.3	~6.1	5.0	4.18			15	~0.5	~0.5	8.5	4.5	6.5	7.0	13	
V=VI	CD_3CN	C_6H_5	C_6H_5	4.56	4.19	6.13	6.28	5.66	4.32	3.71		15.2	~0.5	2.1	8.4	4.6	6.6	7.1	12.4	~1
V and VI(1:20)	HF	C_6H_5	CH_3	4.8	4.4	~6.1		5.7	4.55	4.0	2.4, 2.63 2.9	15.5	~0.5	~1			7	7	13	
V	HF	p-$NO_2C_6H_4$	CH_3	4.4–4.9		5.7–6.3		4.6	4.0		2.35, 2.62 2.9									
V and VI(1:6)	HF	p-$MeOC_6H_4$	CH_3	4.8	4.4	~6		~5.6	4.5	4.0	2.4, 2.6 2.9	15	~0.5	~1			6.5	6.5	13	
V and VI(1:3)	HF	p-MeC_6H_4	C_6H_5								2.47, 2.55 2.60									
V and VI(1:3)	CD_3CN	p-MeC_6H_4	C_6H_5	4.54	4.18	6.08	6.23	5.64	4.31	3.71	2.40 2.52	15.0	~0.5	2.0	8.4	4.5	6.4	7.1	12.3	
VI	CD_3CN	p-$MeOC_6H_4$	C_6H_5	4.50	4.15	5.99	6.14	5.59	4.27	3.69	3.99	14.8	~0.5	2.0	8.2	4.6	6.4	7.1	12.5	~1
V	CD_3CN	p-$NO_2C_6H_4$	C_6H_5	4.59	4.22	6.19	6.36	5.71	4.34	3.76		15.0	~0.5	2.2	8.3	4.6	6.8	7.3	12.5	~1
V and VI(1:1)	HF	p-MeC_6H_4	p-$MeOC_6H_4$								2.43, 2.53 2.62									
V and VI(9:1)	CD_3CN	p-MeC_6H_4	p-$MeOC_6H_4$	4.49	4.15	5.98	6.12	5.57	4.27	3.69	2.39, 2.51 3.84, 3.98	14.9	~0.5	2.0	8.2	4.5	6.5	7.0	12.5	~1

[a] In this table (V) and (VI) are numbered in opposite directions in such a manner that H_3 and H_4 are the protons attached to the dioxolanylium ring in both formulas.

The dibenzoate-*p*-toluate (III, R = *p*-$CH_3C_6H_4$, $R_1 = C_6H_5$) gave a 3:1 mixture of the *p*-methylbenzoxonium ion (VI, R = *p*-$CH_3C_6H_4$, $R_1 = C_6H_5$) and the benzoxonium ion (V). This was seen from the signals at 2.47 and 2.60 ppm (Table 1). A signal at 2.55 ppm showed that *p*-toluic acid was present in the hydrogen fluoride solution. This must be due to exchange of *p*-toluyloxy-groups with benzoic acid, as described above, and formation of some of the benzoxonium ion (V, $R = R_1 = C_6H_5$). The hydrogen fluoride solution was hydrolyzed and the product was washed with base to remove acids. Integrated NMR spectra of the product thus obtained showed that 17 % of the toluyloxy-groups were lost. This must correspond to the amount of ester-exchange that has taken place.

The di-*p*-methoxybenzoate-mono-*p*-toluate (III, R = *p*-$CH_3C_6H_4$, R_1 = *p*-$CH_3OC_6H_4$) gave equal amounts of the ions (V) and (VI) (R = *p*-$CH_3C_6H_4$, R_1 = *p*-$CH_3OC_6H_4$). In this case ester-exchange was also a competing reaction, 20 % of *p*-toluic acid being cleaved off.

In order to avoid the complications caused by exchange reactions the ions (V) and (VI) were prepared in a different manner. It is well known that triphenylmethyl fluoroborate can abstract hydride ions from cyclic aldehyde acetals to give dioxolanylium ions.[5,6] By this method the benzylidene derivatives (IV) could be converted to the ions (V) and (VI) by treatment with triphenylmethyl fluoroborate in acetonitrile at room temperature in the course of 1 – 5 h. The reactions were followed by NMR spectroscopy.

In this way the benzoxonium ion (V, $R = R_1 = C_6H_5$) was obtained from the benzylidene compound (IV, $R = R_1 = C_6H_5$) in 3 – 4 h. The NMR spectrum could be completely analyzed at 100 MHz (Table 1); the corresponding spectrum in hydrogen fluoride was less well resolved. When the nitrobenzoate (IV, R = *p*-$NO_2C_6H_4$, $R_1 = C_6H_5$) was treated with triphenylmethyl fluoroborate the benzoxonium ion (V, R = *p*-$NO_2C_6H_4$, $R_1 = C_6H_5$) was formed as the only product in the course of 3 – 5 h. From the spectral data, presented in Table 1, a distinction between the benzoxonium ion (V) and the nitrobenzoxonium ion (VI) could not be made. However, a complex group of signals in the aromatic region clearly showed that a benzoxonium ion was present since the spectra of such ions are known from previous work.[1] The nitrobenzoxonium ion (VI, R = *p*-$NO_2C_6H_4$, $R_1 = C_6H_5$) would contain a benzoyloxy-group and signals corresponding to this could not be found in the aromatic region.

The *p*-methoxybenzoate (IV, R = *p*-$MeOC_6H_4$, $R_1 = C_6H_5$) gave the methoxybenzoxonium ion (VI, R = *p*-$MeOC_6H_4$, $R_1 = C_6H_5$) as the sole product under the same conditions. This was seen from the δ-value of the methoxy-group which was found to be 3.99, in agreement with the value in hydrogen fluoride (Table 1) and in fluorosulfonic acid.[7] The corresponding value for the methoxybenzoate (IV) was 3.80 and a similar value would be expected for the isomeric ion (V, R = *p*-$MeOC_6H_4$, $R_1 = C_6H_5$).

The two toluates (IV, R = *p*-MeC_6H_4, $R_1 = C_6H_5$) and (IV, R = *p*-MeC_6H_4, R_1 = *p*-$MeOC_6H_5$) both gave mixtures of the two isomeric ions (V) and (VI) (Table 1). The products formed could be identified from the signals of the methyl groups. Those of the *p*-methylbenzoxonium ions (VI) were found at 2.52 and 2.51 ppm, respectively, whereas the *p*-toluyloxy-groups in the isomeric ions (V) gave NMR signals at 2.40 and 2.39 ppm (Table 1).

From these results and from the results obtained in hydrogen fluoride it can be concluded that the stabilities of the dioxolanylium ions (V) and (VI) vary in the following way with the groups attached to C-2 of the dioxolanylium ring: *p*-methoxyphenyl > *p*-methylphenyl > phenyl > methyl > *p*-nitrophenyl. This is of course the range of stabilities that would be expected from inductive and resonance effects. It may be noted that whereas the ions (V) and (VI) ($R_1 = p\text{-}MeOC_6H_4$, $R = p\text{-}MeC_6H_4$) were formed in equal amounts in hydrogen fluoride solution the methoxybenzoxonium ion (V) was found to be more stable than the methylbenzoxonium ion (VI) in acetonitrile (Table 1). This is probably due to a partial protonation of the methoxy-group in hydrogen fluoride, a reaction which will destabilize the methoxybenzoxonium ion (V). The low stability of the *p*-nitrobenzoxonium ion is in agreement with the fact that a *p*-nitrobenzoyl-group shows little tendency to exert a neighbouring group effect in solvolysis reactions.[8]

From the order of stabilities found above it is evident that reaction of unsymmetrically acylated 1,2-cyclohexanediols or cyclopentanediols with hydrogen fluoride [1] leads to formation of the thermodynamically less stable of the two possible dioxolanylium ions.

The 1,5-anhydro-D-arabinitol derivatives (III) were prepared from 3,4-*O*-isopropylidene-1,5-anhydro-D-arabinitol,[9] which by acylation yielded the 2-*O*-acyl-derivatives (I). Hydrolysis of (I) gave the 2-*O*-acyl-1,5-anhydro-D-arabinitols (II), and subsequent diacylation furnished the desired products (III).

The benzylidene derivatives (IV) were obtained by acylation of crude 3,4-*O*-benzylidene-1,5-anhydro-D-arabinitol. Two diastereomeric products (*exo* and *endo*) were obtained in all cases due to asymmetry at the benzylic carbon. The diastereomers were separated and their structures were tentatively assigned from their NMR spectra assuming that the *endo* benzylic protons resonate at lower field than the *exo* protons.[10,11] When the pure isomers were treated with triphenylmethyl fluoroborate they were immediately equilibrated to a mixture of the two diastereomers. Hence a separation of the isomeric pairs is unnecessary.

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. NMR spectra in anhydrous hydrogen fluoride were measured in Teflon sample tubes using $(CH_3)_3SiCH_2CH_2CH_2SO_3Na$ as internal reference.

*1,5-Anhydro-3,4-*O*-isopropylidene-*D*-arabinitol* was prepared according to Hedgley and Fletcher.[8] Alternatively, 1,5-anhydro-D-arabinitol (1.2 g) in acetone (15 ml) was stirred for 20 h with conc. sulfuric acid (0.1 ml) and anhydrous copper sulfate (6 g). Neutralization with barium carbonate, filtration, and evaporation gave the product as a syrup (1.2 g).

*3,4-Di-*O*-acetyl-1,5-anhydro-2-*O*-benzoyl-*D*-arabinitol* (III, $R_1 = CH_3$, $R = C_6H_5$). 1,5-Anhydro-3,4-*O*-isopropylidene-D-arabinitol (3.0 g) was benzoylated with pyridine (10 ml) and benzoyl chloride (2 ml) in the usual way to give 4.1 g of crude (I, $R = C_6H_5$). Crystallization from ethanol gave the pure product (3.34 g), m.p. 101 – 102°C (reported [8] m.p. 102 – 103°C).

The product (553 mg) was suspended in ethanol (10 ml) and 0.8 % sulfuric acid (2 ml). The mixture was then boiled under reflux for 2 h at which time TLC analysis showed that the hydrolysis was complete. The solution was neutralized with barium carbonate, filtered through activated carbon and evaporated. The residue (504 mg) was crystallized from ether-pentane to give pure 1,5-anhydro-2-*O*-benzoyl-D-arabinitol (II, R = C_6H_5), m.p. 96 – 97°C, $[\alpha]_D^{23} = -83.5°$ (*c* 4.0, $CHCl_3$). (Found: C 60.38; H 6.05. Calc. for $C_{12}H_{14}O_5$: C 60.50; H 5.92.)

Acetylation of this product (528 mg) in pyridine (5 ml) with acetic anhydride (1 ml) gave 637 mg of crystalline (III, R = C_6H_5, $R_1 = CH_3$). Recrystallization from ether-pentane gave the pure product, m.p. 92.5 – 93°C, $[\alpha]_D^{23} = -116°$ (*c* 1.5, $CHCl_3$). (Found: C 59.72; H 5.62. Calc. for $C_{16}H_{18}O_7$: C 59.62; H 5.63.)

The other compounds with structures (I), (II), and (III) were prepared by the same procedure. They all gave NMR spectra which were in accordance with their structures.

1,5-Anhydro-3,4-*O*-isopropylidene-D-arabinitol was treated with *p*-nitrobenzoyl chloride in pyridine to give (I, R = *p*-$NO_2C_6H_4$), recrystallized from ether-pentane, m.p. 126 – 127°C. Hydrolysis gave (II, R = *p*-$NO_2C_6H_4$), m.p. 138 – 139°C. Acetylation of this product yielded 3,4-di-*O*-acetyl-1,5-anhydro-2-*O*-*p*-nitrobenzoyl-D-arabinitol (III, R = *p*-$NO_2C_6H_4$, $R_1 = CH_3$) as a syrup which was purified by preparative TLC with ether-pentane (1:2) as eluent, $[\alpha]_D^{23} = -119°$ (*c* 3, $CHCl_3$). (Found: C 52.48; H 4.81. Calc. for $C_{16}H_{17}NO_9$: C 52.31; H 4.67.)

p-Methoxybenzoylation of 1,5-anhydro-3,4-*O*-isopropylidene-D-arabinitol gave (I, R = *p*-$MeOC_6H_4$) which was purified by preparative TLC with ether-pentane (1:1) as eluent; m.p. 68 – 69°C. Hydrolysis as described above yielded (II, R = *p*-$MeOC_6H_4$), m.p. 160 – 161°C. Acetylation finally gave 3,4-di-*O*-acetyl-1,5-anhydro-2-*O*-*p*-methoxybenzoyl-D-arabinitol (III, R = *p*-$MeOC_6H_4$, $R_1 = CH_3$), m.p. 88 – 89°C after recrystallization from ether-pentane, $[\alpha]_D^{23} = -130°$ (*c* 3, $CHCl_3$). (Found: C 58.15; H 5.83. Calc. for $C_{17}H_{20}O_8$: C 57.95; H 5.72.)

Treatment of 1,5-anhydro-3,4-*O*-isopropylidene-D-arabinitol with *p*-toluyl chloride in pyridine gave (I, R = *p*-MeC_6H_4), m.p. 95 – 96°C, after recrystallization from ether-pentane. Hydrolysis gave (II, R = *p*-MeC_6H_4), recrystallized from ether-pentane, m.p. 145 – 147°C. Benzoylation yielded 1,5-anhydro-3,4-di-*O*-benzoyl-2-*O*-*p*-toluyl-D-arabinitol (III, R = *p*-MeC_6H_4, $R_1 = C_6H_5$), crystallized from ether-pentane, m.p. 109 – 110°C, $[\alpha]_D^{23} = -248°$ (*c* 1.6, $CHCl_3$). (Found: C 70.32; H 5.15. Calc. for $C_{27}H_{24}O_7$: C 70.41; H 5.25.)

Treatment of (II, R = *p*-MeC_6H_4) with *p*-methoxybenzoyl chloride in pyridine gave 1,5-anhydro-3,4-di-*O*-*p*-methoxybenzoyl-2-*O*-*p*-toluyl-D-arabinitol (III, R = *p*-MeC_6H_4, R_1 = *p*-$MeOC_6H_4$), m.p. 150 – 151°C, after recrystallization from ethanol, $[\alpha]_D^{23} = -245°$ (*c* 1.3, $CHCl_3$). (Found: C 66.76; H 5.26. Calc. for $C_{29}H_{28}O_9$: C 66.92; H 5.42.)

Benzylidene derivatives (IV). 1,5-Anhydro-D-arabinitol (500 mg), benzaldehyde (400 mg), and *p*-toluenesulfonic acid (10 mg) were dissolved in benzene (25 ml) and heated under reflux with a water-separator until no more water was formed (4 h). The solution was then cooled and neutralized with solid potassium carbonate. Filtration and evaporation gave 900 mg of a colourless syrup which was treated with *p*-toluyl chloride (700 mg) in pyridine (10 ml). Work up in the usual way gave 1.2 g of a product which was separated into two fractions by preparative TLC with ether-pentane (1:1) as eluent. The fast running fraction gave 510 mg (40 %) of a product which was crystallized from ethyl acetate-pentane to give 278 mg (22 %), m.p. 96 – 97°C. The second fraction gave 585 mg (46 %), which was crystallized from ethyl acetate-pentane to give 353 mg (28 %) of a product with m.p. 113 – 114°C. Further data are given in Table 2. The two products are *endo* and *exo* forms of 1,5-anhydro-3,4-*O*-benzylidene-2-*O*-*p*-toluyl-D-arabinitol (IV, R = *p*-$CH_3C_6H_4$, $R_1 = C_6H_5$).

The other products shown in Table 2 were prepared by the same method; they all gave satisfactory NMR spectra.

Reactions with hydrogen fluoride. In order to obtain NMR spectra in hydrogen fluoride solution 150 – 200 mg of the triesters (III) were dissolved in 0.5 – 1.0 ml of anhydrous hydrogen fluoride at 0°C and the solution was poured into a Teflon NMR sample tube. The solutions were kept at 0°C or at room temperature and the spectra were measured at 0°C.

The two esters (III, R = *p*-MeC_6H_4, $R_1 = C_6H_5$) and (III, R = *p*-MeC_6H_4, R_1 = *p*-$MeOC_6H_4$) were kept in hydrogen fluoride solution until no further reactions took place as seen from the NMR spectra (*ca.* 20 h at room temperature). The solutions were then

Table 2. 2-*O*-Acyl-1,5-anhydro-3,4-*O*-benzylidene-D-arabinitols (IV).

Substance R	Substance R_1	*endo* or *exo* H	δ-Value of benzylic proton	M.p. °C	$[\alpha]_D^{21}$ in $CHCl_3$	Analyses C found	Analyses C calc.	Analyses H found	Analyses H calc.	Yield %
C_6H_5	C_6H_5	*endo*	6.29	113–114	−97.3°, *c* 1.5	69.82	69.92	5.43	5.56	30
C_6H_5	C_6H_5	*exo*	5.98	103–104	−134.0, *c* 1.5	70.08	69.92	5.45	5.56	33
C_6H_5	*p*-$NO_2C_6H_4$	*endo*	6.30	92–93	−109.6, *c* 1.6	61.24	61.45	4.65	4.61	13
C_6H_5	*p*-$NO_2C_6H_4$	*exo*	5.97	113–113.5	−147.5, *c* 1.7	61.30	61.45	4.72	4.61	27
C_6H_5	*p*-$MeOC_6H_4$	*endo*	6.28	103–104	−115.3, *c* 1.3	67.26	67.40	5.82	5.66	25
C_6H_5	*p*-$MeOC_6H_4$	*exo*	5.96	114–115	−141.3, *c* 1.6	67.52	67.40	5.72	5.66	33
p-$MeOC_6H_4$	*p*-MeC_6H_4	*endo*	6.25	103–103.5	−99.0, *c* 1.2	67.93	68.09	5.90	5.99	25
p-$MeOC_6H_4$	*p*-MeC_6H_4	*exo*	5.88	128–129	−151.6, *c* 1.1	67.89	68.09	5.97	5.99	22
C_6H_5	*p*-MeC_6H_4	*endo*	6.28	96–97	−109.0, *c* 1.1	70.53	70.57	5.94	5.92	22
C_6H_5	*p*-MeC_6H_4	*exo*	5.89	113–114	−137.7, *c* 1.2	70.58	70.57	6.02	5.92	28

poured onto ice and the products were extracted with methylene chloride. The solutions were washed with aqueous sodium hydrogen carbonate, dried and evaporated. NMR spectra of the products thus obtained showed signals at *ca.* 2 ppm arising from the *p*-toluyloxy-groups. Integration gave information about the amount of ester-exchange that had taken place as described in the discussion.

Reactions in deuterioacetonitrile. The benzylidene esters (IV) (50 – 60 mg) and a 3 – 5 % excess of triphenylmethyl fluoroborate were dissolved in 0.4 ml of deuterioacetonitrile (dried over molecular sieves, 3 Å) in an NMR sample tube which was then closed with a rubber serum cap. The spectra were measured at the probe temperature (*ca.* 33°C).

Analyses were carried out by Dr. A. Bernhardt.

REFERENCES

1. Lundt, I. and Pedersen, C. *Acta Chem. Scand.* **26** (1972) 1938.
2. Pedersen, C. *Tetrahedron Letters* **1967** 511.
3. Hedgley, E. J. and Fletcher, H. G., Jr. *J. Am. Chem. Soc.* **85** (1963) 1615.
4. Paulsen, H. *Advan. Carbohyd. Chem. Biochem.* **26** (1971) 127.
5. Paulsen, H. and Behre, H. *Chem. Ber.* **104** (1971) 1281.
6. Meerwein, H., Hederich, V., Morschel, H. and Wunderlich, K. *Ann. Chem.* **635** (1960) 1.
7. Tomalia, D. A. and Hart, H. *Tetrahedron Letters* **1966** 3389.
8. Glaudemans, C. P. J. and Fletcher, H. G., Jr. *J. Am. Chem. Soc.* **87** (1965) 2456.
9. Hedgley, E. J. and Fletcher, H. G., Jr. *J. Org. Chem.* **30** (1965) 1282.
10. Baggett, N., Buck, K. W., Foster, A. B. and Webber, J. M. *J. Chem. Soc.* **1965** 3401.
11. Inch, T. D. *Carbohyd. Res.* **21** (1972) 37.

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