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DIFFERENT REACTIVITIES OF ACETYLATED *exo*- AND *endo*-CYANOETHYLIDENE DERIVATIVES IN GLYCOSYLATION REACTIONS

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ABSTRACT

The condensation of acetylated 1-(*endo*-cyano)ethylidene derivatives having the D-*gluco*, D-*xylo*, and D-*galacto* configurations (**2–6**) with a primary (**8**) and a secondary (**9**) trityl derivative was more rapid than for the corresponding *exo*-isomers. This difference in reactivity is explained on the basis of differences in conformation.

INTRODUCTION

As part of a project on the syntheses of chiral molecular receptors[1], diglycosyl derivatives of ethylene glycol such as **1** were needed. The preparation of these compounds was attempted using the trityl–cyanoethylidene condensation[2], which has been reported to be an effective stereoselective glycosylation procedure. When the trityl–cyanoethylidene condensation[2] was applied to the 1,2-di-*O*-trityl derivative (**8**) of ethylene glycol under conditions modified to avoid the use of a vacuum technique, a remarkable difference in reactivity between 3,4,6-tri-*O*-acetyl-1,2-*O*-[1-(*exo*- and *endo*-cyano)ethylidene]-α-D-glucopyranose[3] (**2** and **3**) was observed. We now report on this observation and on its generalization using various *exo* and *endo* cyanoethylidene derivatives and different tritylated compounds.

RESULTS AND DISCUSSION

The reaction of 2 mol of 3,4,6-tri-*O*-acetyl-1,2-*O*-[1-(*exo*-cyano)ethylidene]-α-D-glucopyranose (**2**) with 1 mol of **8** in dichloromethane under argon in the presence of tritylium tetrafluoroborate afforded 1,2-bis(2,3,4,6-*tetra*-*O*-acetyl-β-D-glucopyranosyloxy)ethane (**1**; 29% after 5 h), ~10% of **2** was recovered, and there were some decomposition products formed probably due to traces of water. A parallel reaction with the *endo*-isomer (**3**) gave a similar yield of **1** after 2 h. This difference in reactivity of *exo*- and *endo*-cyanoethylidene derivatives has not been

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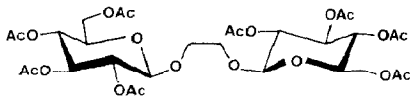

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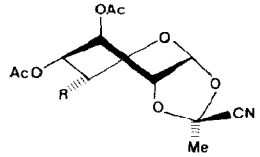

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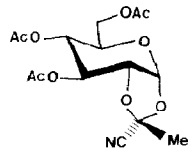
4 R = H



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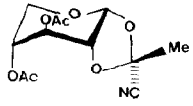

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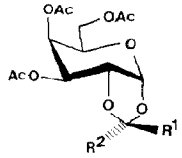
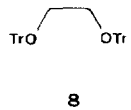


6 R^1 = CN , R^2 = Me

7 R^1 = Me , R^2 = CN



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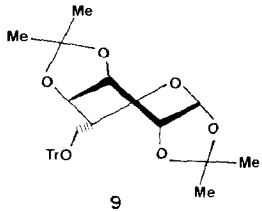

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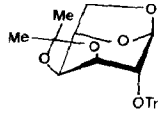

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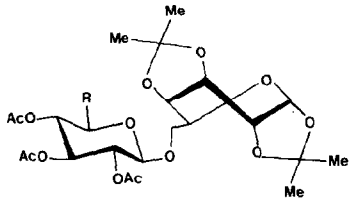
reported hitherto, probably because vacuum[4] or high-pressure[5] techniques were used, although condensation without recourse to the vacuum technique has been described[5c]. The *exo*-cyano- (**2**) and *endo*-cyano-ethylidene (**3**) derivatives have different conformations in the solid state and in solution[6]; the conformations[7] of the pyranoid and dioxolane rings are $^{o}S_2$ and E_{o3} for **2**, and $^{4}C_1$ and $^{o2}T_3$ for **3**. In seeking to relate conformation and reactivity, the reaction of 1-(*exo*- and *endo*-cyano)ethylidene derivatives of D-gluco- (**2** and **3**), D-xylo- (**4** and **5**), and D-galacto-pyranose (**6** and **7**), which show different conformational properties, with trityl derivatives of different reactivity was studied.

When **2** and **3** reacted with 1,2:3,4-di-*O*-isopropylidene-6-*O*-trityl-α-D-galacto-pyranose (**9**) under the above conditions, 54% of 1,2:3,4-di-*O*-isopropylidene-6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-galactopyranose (**11**) was obtained after 3.5 and 1.5 h, respectively. Similarly, reactions of **2** and **3** with 1,6-anhydro-3,4-*O*-isopropylidene-2-*O*-trityl-α-D-galactopyranose (**10**) afforded 30% of 1,6-anhydro-3,4-*O*-isopropylidene-2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-β-D-galactopyranose (**13**) after 4 h and 1 h 50 min, respectively.



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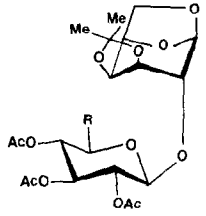
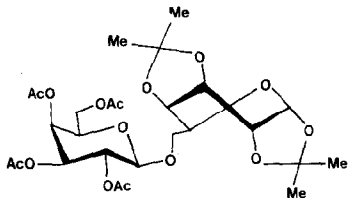
12 R = H



13 R = CH_2OAc

14 R = H



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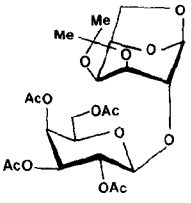

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The major conformations of the pyranoid and acetal rings of 3,4-di-*O*-acetyl-1,2-*O*-[1-(*exo*-cyano)ethylidene]-α-D-xylopyranose (**4**) are $^{o}S_2$ and E_{o2} in solution, and $^1C_4$ and ^2E in the solid state[8] whereas those for the *endo*-isomer **5** are $^1C_4$ and E_1 in both solution and the solid state[8]. The reaction of **4** and **5** with **9** gave 60% of 1,2:3,4-di-*O*-isopropylidene-6-*O*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-α-D-galactopyranose (**12**) after 1.5 and 1 h, respectively. Similarly, reaction of **4** and **5** with **10** afforded only 27% of 1,6-anhydro-3,4-*O*-isopropylidene-2-*O*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-β-D-galactopyranose (**14**) in 1 h 45 min and 1 h 10 min, respectively.

The pyranoid rings of 3,4,6-tri-*O*-acetyl-1,2-*O*-[1-(*exo*- and *endo*-cyano)-ethylidene]-α-D-galactopyranose (**6** and **7**) have the $^4C_1$ conformation both in the solid state and in solution[6b,9]. For the dioxolane ring in **6**, there is a conformational equilibrium $^1E \rightleftharpoons {}^1T_1$ in solution[7], and $^1E \rightleftharpoons {}^1T_2$ for **7** (E_1 in the solid state[6b]). Reaction of **6** and **7** with **9** gave 65% of 1,2:3,4-di-*O*-isopropylidene-6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-galactopyranose (**15**) after 3 h and 1 h 10 min, respectively. Similarly, the reaction of **6** and **7** with **10** afforded 26% of 1,6-anhydro-3,4-*O*-isopropylidene-2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-galactopyranose (**16**) after 3 h and 1 h 15 min, respectively.

The differences in reactivity noted above may be explained in terms of steric accessibility of the anomeric center of the cyanoethylidene derivatives. Nucleophilic attack on C-1 is hindered in the *exo*-isomer **2** due to the 1,3-interaction of

AcO-3 and the *exo*-cyano group, which is pseudo-axial due to the tendency of the methyl group to occupy a pseudo-equatorial orientation[7,9]. These unfavourable interactions are absent from the *endo*-isomer **3**. The same arguments hold for the xylopyranose derivatives **4** and **5**, although the absence of a 5-substituent, which results in greater flexibility of the pyranoid ring, together with unfavourable 1,3 interaction in the *endo*-isomer (**5**), reduces the difference in reactivity.

For the *exo*-D-*galacto* derivative **6**, the unfavourable 1,3-interaction associated with the *exo*-cyano group, which is absent from *endo*-isomer **7**, is responsible for the differences in reactivity.

It is generally assumed that the trityl–cyanoethylidene condensation involves a concerted mechanism[2]. When the condensation was monitored by ^{1}H-n.m.r. spectroscopy, no signals for Me in acyloxonium ions or for the α-glycoside were detected, thus supporting the concerted mechanism.

Partial detritylation of the tritylated alcohols could be observed during the glycosylation reaction probably due to the presence of traces of water. Partial detritylation was also observed when **9** and **10** were treated with tritylium tetrafluoroborate in the absence of cyanoethylidene derivative. ^{1}H-N.m.r. spectroscopy and t.l.c. then showed that an equilibrium between tritylated and detritylated alcohols was established. Examples of tritylation and detritylation of alcohols in dichloromethane with triphenylmethylium perchlorate or tetrafluoroborate have been reported[11].

In spite of this side-reaction, glycosylation proceeds with the alcohol, as demonstrated in the reaction of **5** with the detritylated derivative of **9** to give **12**.

EXPERIMENTAL

General methods. — Melting points were determined on a Kofler hot-stage and are uncorrected. Column chromatography was performed on silica gel (70–230 mesh, Merck), and t.l.c. on Silica Gel 60 F_{254} (Merck) with detection by charring with sulfuric acid. The ^{1}H- and ^{13}C-n.m.r. spectra were recorded for solutions in $CDCl_3$, using a Varian XL-300 or Bruker AM-200 spectrometer. Optical rotations were measured with a Perkin–Elmer 141 polarimeter. Compounds **2–7** were prepared by methods in the literature[3,12]. The preparation of **8** and **9** has been reported[13,14].

*1,6-Anhydro-3,4-O-isopropylidene-2-O-trityl-β-*D*-galactopyranose* (**10**). — A mixture of 1,6-anhydro-3,4-*O*-isopropylidene-β-D-galactopyranose (250 mg, 1.23 mmol), trityl chloride (517 mg, 1.85 mmol), and 4-dimethylaminopyridine in dry pyridine (15 mL) was stirred for 3 days at 40°, then filtered, and concentrated. Column chromatography (hexane–ethyl acetate, 3:1) of the residue gave **10** (360 mg, 65%), m.p. 169–170°, $[\alpha]_D$ −66° (*c* 0.9, chloroform). N.m.r. data: ^{1}H, δ 7.45–7.42 (m, 5 H, Ph), 7.35–7.19 (m, 10 H, 2 Ph), 5.15 (s, 1 H, H-1), 4.42 (t, 1 H, H-5), 4.28 (t, 1 H, H-4), 3.96–3.92 (d, 1 H, H-6*endo*), 3.89 (s, 1 H, H-2), 3.50–3.42 (m, 2 H, H-3,6*exo*), 1.37, 0.95 (2 s, each 3 H, CMe_2); ^{13}C, 143.8, 128.9, 128.6, 128.3,

128.0, 127.8, 127.9 (aromatic), 107.8 (CMe_2), 101.1 (C-1), 88.2 (Ph_3C), 74.8, 72.1, 71.9, 69.2, 63.0, 25.7, and 24.2.

Anal. Calc. for $C_{28}H_{28}O_5$: C, 75.67; H, 6.30. Found: C, 75.58; H, 6.60.

Glycosylation reactions. — A solution of triphenylmethylium tetrafluoroborate (0.058 mmol) in dry CH_2Cl_2 (0.5 mL) was added to a stirred mixture of cyanoethylidene derivative (0.2 mmol) and trityl ether (0.2 mmol) in dry CH_2Cl_2 (2 mL) under argon. The solution was stirred at 40° until the reaction was complete (t.l.c.). Dry methanol (0.5 mL) was added followed by 2 drops of pyridine, the mixture was concentrated, and the residue was washed with hexane. The β-glycoside, unreacted cyanoethylidene derivative (~10%), and low-mobility products were obtained. For **1**, 2 mol of **2** or **3** were used per mol of **8**.

1,2:3,4-Di-O-isopropylidene-6-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-α-D-galactopyranose (**11**). — Compound **11** was obtained from **2** and **9** in 3.5 h and from **3** and **9** in 1.5 h. Column chromatography (hexane–ethyl acetate, 7:5) gave **10** (54%), m.p. 138–140°, $[\alpha]_D$ −54° (*c* 0.7, chloroform); lit.[15] m.p. 140–142°, $[\alpha]_D$ −54.5°.

1,6-Anhydro-3,4-O-isopropylidene-2-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-β-D-galactopyranose[16] (**13**). — For reaction times and yield, see text. Column chromatography (hexane–ethyl acetate, 7:5) gave **13** as a syrup, $[\alpha]_D$ −29° (*c* 0.6, chloroform).

1,2:3,4-Di-O-isopropylidene-6-O-(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-α-D-galactopyranose (**12**). — For reaction times and yield, see text. Column chromatography (hexane–ethyl acetate, 3:1) gave **12**, m.p. 124–125°, $[\alpha]_D$ −79° (*c* 0.47, chloroform). N.m.r. data: ^1H, δ 5.51 (d, 1 H, $J_{1,2}$ 4.9 Hz, H-1), 5.18 (dd, 1 H, $J_{2',3'} \approx J_{3',4'} \approx 8.6$ Hz, H-3'), 4.95 (dt, 1 H, $J_{4',5'e}$ 5.1 Hz, H-4'), 4.94 (dd, 1 H, $J_{2',1'}$ 6.8 Hz, H-2'), 4.60 (dd, 1 H, $J_{2,3}$ 2.5, $J_{3,4}$ 8 Hz, H-3), 4.59 (d, 1 H, H-1'), 4.31 (dd, 1 H, H-2), 4.20 (dd, 1 H, $J_{4,5}$ 1.5 Hz, H-4), 4.13 (dd, 1 H, $J_{5'e,5'a}$ 11.8 Hz, H-5'*e*), 4.00–3.92 (m, 2 H, H-6a,6b), 3.67 (dt, 1 H, H-5), 3.37 (dd, 1 H, $J_{5'a,4'}$ 8.7 Hz, H-5'*a*), 2.08, 2.05, 2.04 (3 s, 9 H, 3 Ac), 1.52, 1.45, 1.33 (3 s, 12 H, 2 CMe_2); ^{13}C, 169.9–169.5 (CO), 109.3, 108.5 (CMe_2), 101.2 (C-1'), 96.2 (C-1), 71.3, 71.1, 70.6 (d), 70.4, 68.9, 68.6, 67.4, 61.9, 26.0, 25.9, 24.9, 24.3, and 20.6.

Anal. Calc. for $C_{23}H_{34}O_{13}$: C, 53.27; H, 6.60. Found: C, 53.40; H, 6.90.

1,6-Anhydro-3,4-O-isopropylidene-2-O-(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-β-D-galactopyranose (**14**). For reaction times and yield, see text. Column chromatography (hexane–ethyl acetate, 3:1) gave **14** as a syrup, $[\alpha]_D$ −64° (*c* 0.25, chloroform). N.m.r. data: ^1H, δ 5.48 (s, 1 H, H-1), 5.15 (t, 1 H, $J_{2',3'} \approx J_{3',4'} \approx 8.5$ Hz, H-3'), 4.95 (dt, 1 H, $J_{3',4'} \approx J_{4',5'a} \approx 8.6$, $J_{4',5'e}$ 5.0 Hz, H-4'), 4.92 (dd, 1 H, $J_{1',2'}$ 6.6 Hz, H-2'), 4.65 (d, 1 H, H-1'), 4.49 (t, 1 H, H-5), 4.39 (t, 1 H, H-4), 4.14 (dd, 1 H, $J_{5'e,5'a}$ 11.8 Hz, H-5'*e*), 4.06 (d, 2 H, $J_{3,4} \approx J_{6a,6b} \approx 7.6$ Hz, H-3,6), 3.77 (s, 1 H, H-2), 3.56 (dd, 1 H, $J_{6,5}$ 5.2 Hz, H-6), 3.38 (dd, 1 H, H-5'*a*), 2.05, 2.04, 2.03 (3 s, each 3 H, 3 Ac), 1.52, 1.34 (2 s, each 3 H, CMe_2); ^{13}C, 169.9–169.03 (CO), 108.5 (CMe_2), 100.4 (anomeric C), 100.0 (anomeric C), 77.5, 74.9, 71.6, 71.0, 70.6, 68.9, 68.4, 62.8, 61.9, 25.4, 24.0, and 20.5.

Anal. Calc. for $C_{20}H_{28}O_{12}$: C, 52.17; H, 6.12. Found: C, 52.4; H, 6.40.

1,2:3,4-Di-O-isopropylidene-6-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-α-D-galactopyranose (**15**). — For reaction times and yield, see text. Column chromatography (hexane–ethyl acetate, 3:1) gave **15**, m.p. 105–106°, $[\alpha]_D$ −44° (*c* 0.4, chloroform); lit.[17] m.p. 101–102°, $[\alpha]_D$ −44.7°.

1,6-Anhydro-3,4-O-isopropylidene-2-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-β-D-galactopyranose (**16**). — For reaction times and yield, see text. Column chromatography (hexane–ethyl acetate, 3:1) gave **16**, m.p. 128–130°, $[\alpha]_D$ −15° (*c* 0.54 chloroform). N.m.r. data: ^{1}H, δ 5.54 (s, 1 H, H-1), 5.38 (dd, 1 H, $J_{4',5'}$ 1.1, $J_{3',4'}$ 3.4 Hz, H-4'), 5.22 (d, 1 H, $J_{1',2'}$ 7.8, $J_{2',3'}$ 10.4 Hz, H-2'), 5.03 (dd, 1 H, H-3'), 4.63 (d, 1 H, H-1'), 4.53–4.36 (dt, 2 H, H-4,5), 4.16–4.05 (m, 4 H, H-3,6*endo*,6'a,6'b), 3.96–3.89 (m, 1 H, H-5'), 3.78 (s, 1 H, H-2), 3.58–3.56 (m, 1 H, H-6*exo*); ^{13}C, 170.3–169.0 (CO), 108.6 (CMe_2), 101.5 (anomeric C), 100.2 (anomeric C), 78.8, 74.8, 71.8, 71.0, 70.8, 69.2, 68.9, 66.9, 63.0, 61.3, 25.7, 24.1, 20.6, and 20.5.

Anal. Calc. for $C_{23}H_{32}O_{14}$: C, 51.87; H, 6.05. Found: C, 51.99; H, 6.26.

1,2-Bis(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyloxy)ethane (**1**). — See text, for reaction times and yield. Column chromatography (hexane–ethyl acetate, 1:1) gave **1**, $[\alpha]_D$ −7° (*c* 0.8, chloroform). N.m.r. data: ^{1}H, δ 5.23 (t, 1 H, $J_{2,3} \approx J_{3,4} \approx$ 9.5 Hz, H-3), 5.09 (t, 1 H, $J_{4,5}$ 9.7 Hz, H-4), 4.98 (dd, 1 H, $J_{1,2}$ 7.8, $J_{2,3}$ 9.5 Hz, H-2), 4.59 (d, 1 H, H-1), 4.28 (dd, 1 H, $J_{5,6}$ 4.6, $J_{6a,6b}$ 12.5 Hz, H-6), 4.13 (dd, 1 H, $J_{5,6}$ 2.4 Hz, H-6), 3.92 (d, 1 H, *J* 9.0 Hz, OCH_2CH_2O), 3.79 (d, 1 H, *J* 8.98 Hz, OCH_2CH_2O), 3.71 (m, 1 H, H-5), 2.09, 2.08, 2.03, 2.00 (4 s, each 3 H, 4 Ac); ^{13}C, 170.6–169.4 (CO), 100.4 (C-1), 72.6, 71.7, 71.3, 68.5, 68.3, 61.7, 20.7, 20.6, and 20.5.

Anal. Calc. for $C_{30}H_{42}O_{20}$: C, 49.84; H, 5.86. Found: C, 49.92; H, 5.91.

Detritylation of **9** *and* **10**. - To a solution of trityl ether (0.2 mmol) in dry dichloromethane (2.5 mL) under argon was added a solution of trityl tetrafluoroborate (17.7 mg, 0.053 mmol) in dichloromethane (0.5 mL). The formation of the corresponding alcohol was followed by t.l.c.

Glycosylation of the alcohol. — A solution of trityl tetrafluoroborate (17.7 mg, 0.053 mmol) in dry dichloromethane (0.5 mL) was added to a stirred mixture of **5** (57 mg, 0.2 mmol) and 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (65 mg, 0.25 mmol) in dichloromethane (2 mL) under argon. The solution was stirred at 40°, and the formation of **9** and glycoside **12** was followed by t.l.c.

ACKNOWLEDGMENTS

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