SUCROCHEMISTRY

PART VI[1]. FURTHER REACTIONS OF 6,6′-DI-*O*-TOSYLSUCROSE AND A COMPARISON OF THE REACTIVITY AT THE 6 AND 6′ POSITIONS

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ABSTRACT

Reaction of 6,6′-di-*O*-tosylsucrose hexa-acetate (**1**) with sodium chloride in hexamethylphosphoric triamide gave a mixture containing preponderantly the hexa-acetates of 6,6′-dichloro-6,6′-dideoxysucrose (**2**) and 6-chloro-6-deoxy-6′-*O*-tosylsucrose (**3**). Reaction of **3** with sodium benzoate in $(Me_2N)_3PO$ gave the 6-chloro-6-deoxy-6′-*O*-benzoyl derivative **4**. Subsequent *O*-de-esterification afforded syrupy 6-chloro-6-deoxysucrose (**5**), which gave a crystalline heptamethanesulphonate. The chloro groups in the heptabenzoate **7** and the hexa-acetate **2** were replaced by azide in $(Me_2N)_3PO$ to give the corresponding derivatives of 6-azido-6-deoxysucrose (**12**) and 6,6′-diazido-6,6′-dideoxysucrose (**8**), respectively. *O*-De-esterification of the hexa-acetates **2** and **8** yielded the parent 6,6′-dichloride **6** and 6,6′-diazide **9**, respectively. 6,6′-Di-*O*-tosylsucrose hexabenzoate (**10**) reacted with sodium bromide in $(Me_2N)_3PO$ to give the 6,6′-dibromide **11**, in high yield, which afforded 6-deoxy-β-D-*xylo*-hex-5-enopyranosyl 6′-deoxy-β-D-*threo*-hex-5′-enofuranoside hexabenzoate on treatment with silver fluoride in pyridine.

INTRODUCTION

During the benzoylation of 6,6′-di-*O*-tosylsucrose at room temperature with benzoyl chloride in pyridine, significant quantities of a monochloro-monodeoxysucrose (16%) and 6,6′-dichloro-6,6′-dideoxysucrose (7%) were isolated[2]. A difference in the reactivities at C-6 and C-6′ thus revealed was also noted in transesterification reactions of sucrose[3,4]. Consequently, we have studied the nucleophilic substitution of the 6,6′-di-*O*-tosyl derivative **1** by chloride and bromide ions in $(Me_2N)_3PO$ with a view to obtaining an improved yield of mono- and di-halogeno derivatives and determining the order of reactivity of C-6 and C-6′. Since facile syntheses of chlorodeoxy sugars[5], including sucrose[6], have been reported, and also their substitution by azide[7], we have examined the azide replacement of the chloro substituents on sucrose derivatives as an alternative to the route *via* toluene-*p*-sulphonates.

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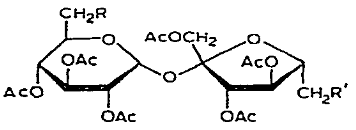
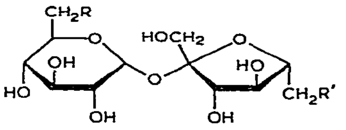
RESULTS AND DISCUSSION

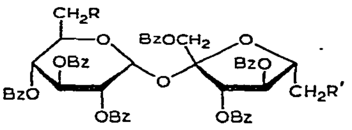
The direct preparation of chlorodeoxy derivatives of sucrose by reaction of sucrose with tosyl chloride in *N*,*N*-dimethylformamide[8] was tried without success. The reaction of 6,6′-di-*O*-tosylsucrose hexa-acetate (**1**) with sodium chloride in $(Me_2N)_3PO$ at 85° was stopped after 14 h when mono-substitution appeared to be optimal, as judged by t.l.c. The two major products were separated on silica gel, the faster being the expected crystalline 6,6′-dichloride **3** (51%), and the slower a syrupy monochloro-monodeoxy-mono-*O*-tosylsucrose hexaacetate (34%). The n.m.r. spectrum of the latter was consistent with its structure, and a sharp doublet for the H-1 signal was indicative of its purity. Replacement of the sulphonate group of the latter compound by treatment with sodium benzoate in $(Me_2N)_3PO$ gave a syrupy monochloro-mono-*O*-benzoyl derivative. Subsequent *O*-de-esterification afforded syrupy 6-chloro-6-deoxysucrose (**5**) which was characterised as the crystalline heptamethanesulphonate. Cautious hydrolysis of **5** gave (paper chromatography) fructose and 6-chloro-6-deoxyglucose. Hence, the 6-*O*-tosyl group of the D-glucopyranoid unit of 6,6′-di-*O*-tosylsucrose is more reactive towards nucleophilic substitution than the 6′-*O*-tosyl group of the D-fructofuranoid unit, as would be anticipated from conformational considerations of the respective transition states[9]. Comparisons of the reactivities at the 6- and 6′-positions of sucrose towards transesterification led to the same conclusion[3]. The introduction of chloro substituents at C-6 and C-6′ of sucrose has little effect upon their rates of hydrolysis.



1 R = R′ = OTs
2 R = R′ = Cl
3 R = Cl, R′ = OTs
4 R = Cl, R′ = OBz
8 R = R′ = N_3



5 R = Cl, R′ = OH
6 R = R′ = Cl
9 R = R′ = N_3



7 R = Cl, R′ = OBz
10 R = R′ = OTs
11 R = R′ = Br
12 R = N_3, R′ = OBz

The reaction of 6,6′-di-*O*-tosylsucrose hexabenzoate with sodium bromide in $(Me_2N)_3PO$ at 85° proceeded more rapidly than with the chloride, and after 6 h the 6,6′-dibromide (**11**) was isolated in 87% yield. Like the 6,6′-di-iodo derivative[2], the dibromide **11**, on treatment with silver fluoride in pyridine, afforded the 5,5′-diene by elimination of hydrogen bromide.

Replacement of the chloro substituents in the 6,6′-dichloride **2** by azide was readily achieved in $(Me_2N)_3PO$, although accompanied by some *O*-deacetylation; re-acylation afforded the 6,6′-diazide **8** in 84% yield. 6-Azido-6-deoxysucrose heptabenzoate (**12**) was prepared similarly from the 6-chloride[2] **7**, but *O*-debenzoylation was insignificant.

EXPERIMENTAL

General. — All evaporations were carried out under reduced pressure. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Optical rotations were measured on a Perkin–Elmer 141 polarimeter in 1 dm tubes. Column chromatography on silica gel was carried out at room temperature using Mallinckrodt "Silic AR" c.c.4. (100–200 mesh). Thin-layer and preparative layer chromatography was performed at room temperature on silica gel (Merck, 7731). The separated materials were detected by spraying the dried chromatograms with a 5% solution of conc. H_2SO_4 in ethanol and heating at 110–115° for 3–6 min. Dry $(Me_2N)_3PO$ was prepared by storage over a molecular sieve for several days and then distillation under reduced pressure. N.m.r. spectra were measured for solutions in acetone-d_6 at 100 MHz (Varian HA-100) with tetramethylsilane as internal standard.

Treatment of 6,6'-di-O-tosylsucrose hexa-acetate (**1**) *with sodium chloride in hexamethylphosphoric triamide.* — Sodium chloride (7.0 g) was added to a solution of **1** (7.0 g) in $(Me_2N)_3PO$ (21 ml). The reaction mixture was heated at 85° with stirring, examined hourly by t.l.c. (ether–light petroleum, 6:1), and stopped after 14 h when two products moving faster than the starting material were present. The cooled reaction mixture was then poured into ice–water, and the white precipitate was filtered off, washed well with water, dried (phosphoric oxide), and then eluted from silica gel (400 g) with ether–light petroleum (3:1). The following products were obtained: (*a*) 6,6'-Dichloro-6,6'-dideoxysucrose hexa-acetate (**2**), the faster moving fraction (2.5 g, 51%), m.p. 117–118° (from ether–light petroleum), $[\alpha]_D^{28}$ +55° (*c* 0.55, chloroform) (Found: C, 45.7; H, 5.4; Cl, 10.9. $C_{24}H_{32}Cl_2O_5$ calc.: C, 45.6; H, 5.1; Cl, 11.1). N.m.r. data: τ 4.3 (*d*, 1 proton, $J_{1,2}$ 3.5 Hz, H-1), 5.14 (*q*, 1 proton, $J_{2,3}$ 10.0 Hz, H-2), 4.54 (*t*, 1 proton, $J_{3,4}$ 10.0 Hz, H-3), 4.9 (*t*, 1 proton, $J_{4,5}$ 10.0 Hz, H-4), 4.5 (*d*, 1 proton, $J_{3',4'}$ 5.5 Hz, H-3'), 4.58 (*t*, 1 proton, $J_{4',5'}$ 5.5 Hz, H-4'). (*b*) 6-Chloro-6-deoxy-6'-*O*-tosylsucrose hexa-acetate (**3**), a syrup (2.0 g, 34%), $[\alpha]_D^{30}$ +54° (*c* 1.0, chloroform) (Found: C, 48.5; H, 5.3; Cl, 4.4; S, 4.6. $C_{31}H_{39}ClO_{18}S$ calc.: C, 48.5; H, 5.3; Cl, 4.6; S, 4.2). N.m.r. data: τ 4.4 (*d*, 1 proton, $J_{1,2}$ 3.5 Hz, H-1), 5.2 (*q*, 1 proton, $J_{2,3}$ 10 Hz, H-2), 4.68 (*t*, 1 proton, $J_{3,4}$ 10 Hz, H-3), 4.98 (*t*, 1 proton, $J_{4,5}$ 10 Hz, H-4), 4.54 (*d*, 1 proton, $J_{3',4'}$ 6.5 Hz, H-4'), 7.86–8.10 (*m*, 18 protons, 6Ac). The remaining resonances could not be interpreted, due to overlapping.

6,6'-Dichloro-6,6'-dideoxysucrose (**6**). — A solution of the hexa-acetate **2** (1.0 g) in dry methanol (20 ml) was treated with M methanolic sodium methoxide (1 ml) and kept at room temperature for 5 h. T.l.c. (ethanol–chloroform, 3:5; or 1-butanol–acetic acid–water, 12:3:5) showed one product running slower than the starting matrial. The solution was neutralised with Amberlite IRC-50 (H^+) resin (previously washed with methanol). The resin was filtered off and the filtrate concentrated to a syrup which crystallised from butanone to give **6** (0.49 g, 81%), m.p. 85–88°, $[\alpha]_D^{25}$ +60° (*c* 0.50, water) (Found: C, 37.2; H, 5.7; Cl 18.1. $C_{12}H_{20}Cl_2O_9$ calc.: C, 37.9; H, 5.3; Cl, 18.7%). A solution of **6** in 0.5M hydrochloric acid (2 ml) had $[\alpha]_D^{24}$ +55.6° (initial)→ +42.4° (12 h, constant value).

6′-O-Benzoyl-6-chloro-6-deoxysucrose hexa-acetate (**4**). — Sodium benzoate (1 g) was added to a solution of **3** (1.0 g) in $(Me_2N)_3PO$ (4 ml) and heated at 85° with stirring for 20 h. T.l.c. (ether–light petroleum, 4:1) then showed the presence of a major product running faster than the starting material. The cooled reaction mixture was poured into ice–water, and the white precipitate was filtered off, washed with water, and then dissolved in acetone. The dried ($MgSO_4$) solution was concentrated, and acetylation of the residue in dry pyridine (10 ml) with acetic anhydride (10 ml) gave a syrup which was purified by p.l.c. (ether–light petroleum, 4:1), using iodine vapour to locate the products. The syrupy monobenzoate **4** was dried in vacuum over phosphoric oxide and paraffin wax; yield 400 mg (43%), $[\alpha]_D^{28}$ +61.9° (*c* 0.1, chloroform) (Found: C, 51.6; H, 5.3; Cl, 0.7. $C_{31}H_{37}ClO_{17}$ calc.: C, 51.9; H, 5.2; Cl, 0.5%).

6-Chloro-6-deoxysucrose (**5**). — A solution of **4** (300 mg) in dry methanol (20 ml) was treated with 2M methanolic sodium methoxide (0.3 ml) for 4 h at room temperature. T.l.c. (1-butanol–acetic acid–water, 12:3:5; and chloroform–ethanol, 5:3) then showed a major product with two minor constituents. The R_F value of the major product was intermediate between those of sucrose and 6,6′-dichloro-6,6′-dideoxysucrose (**6**). The reaction mixture was neutralised with Amberlite resin IRC-50 (H^+) (previously washed with methanol) and concentrated to a syrup. The syrup was boiled with light petroleum which was then decanted carefully, and this operation was repeated several times to remove all of the methyl acetate and methyl benzoate. The de-acetylated product was purified by p.l.c. (chloroform–ethanol, 5:3; detection with iodine). A solution of the required product in methanol was filtered through "Hyflo Supercel" and concentrated *in vacuo* to give syrupy 6-chloro-6-deoxysucrose (**5**, 75 mg, 50%), $[\alpha]_D^{23}$ +55° (*c* 1.0, water). A solution of **5** in 0.5M hydrochloric acid had $[\alpha]_D^{24}$ +50° (initial)→+24° (5 h, constant value).

A solution of **5** (25 mg) in dry pyridine (10 ml) was cooled to 0° and mesyl chloride (0.8 ml) added dropwise over a period of 8 min. The reaction mixture was stirred at room temperature for 16 h. T.l.c. (chloroform–acetone, 3:2) then showed a major product which had the same R_F value as the monochloro derivative prepared by the direct reaction of octa-*O*-mesylsucrose[10] with sodium chloride. The reaction mixture was concentrated, and pyridine was removed by co-distillation with toluene. A solution of the resulting syrup in chloroform was washed three times with water, dried ($MgSO_4$), and concentrated to yield a brown syrup. 6-Chloro-6-deoxysucrose heptamethanesulphonate (50 mg, 80%) was isolated by p.l.c. (chloroform–acetone 3:2; detection with iodine), m.p. 99–101° (from methanol), $[\alpha]_D^{25}$ +50° (*c* 0.15, acetone) (Found: C, 25.2; H, 4.2; Cl, 4.7. $C_{19}H_{35}ClO_{24}S_7$ calc.: C, 25.1; H, 3.9; Cl, 3.9%). N.m.r. data: τ 3.9 (*d*, 1 proton, $J_{1,2}$ 3.0 Hz, H-1), 5.0 (*q*, 1 proton, $J_{2,3}$ 11.0 Hz, H-2), 4.1 (*d*, 1 proton, $J_{3',4'}$ 8.0 Hz, H-3′), 4.4 (*t*, 1 proton, $J_{4',5'}$ 8.0 Hz, H-4′). The remaining resonances could not be interpreted.

*6-Chloro-6-deoxy-*D*-glucose.* — A solution of methyl 6-chloro-6-deoxy-α-D-glucopyranoside[8] (1.0 g) in 5% hydrochloric acid (25.0 ml) was heated to 95° for 6 h with stirring, after which time t.l.c. (chloroform–methanol, 3:1) showed one major product moving slower than the starting material. The neutralised (lead carbonate) solution was concentrated, and a solution of the syrupy residue in methanol was dried ($MgSO_4$) and concentrated to small volume. The required product was isolated by p.l.c. (chloroform–methanol 3:1), using iodine vapour for detection. 6-Chloro-6-deoxy-D-glucose was obtained as a hygroscopic, semi-crystalline syrup (747 mg, 80%), $[\alpha]_D^{25}$ +46° (*c* 1.03, water); lit.[11] $[\alpha]_D$ +46.6° (equil., water).

Acid hydrolysis of 6-chloro-6-deoxysucrose (**5**). — A solution of **5** (10 mg) in M hydrochloric acid (10 ml) was stirred for 10 h at room temperature, and then neutralised with Amberlite IR-45 (HO^-) resin and concentrated at 40° to a small volume.

Ascending-front, paper chromatography of the hydrolysate was carried out (Whatman No. 1 paper) by using multiple development with 1-propanol–ammonia–water (6:3:1) and incorporating 6-chloro-6-deoxy-D-glucose as a reference substance (R_S 1.0). After three developments, the chromatogram was dried, sprayed with a solution of *p*-aminophenol (0.5 g) and orthophosphoric acid (2.0 g) in ethanol (50 ml), and then heated for 5 min at 105–110°. The R_S values of sucrose, D-glucose, D-fructose, 6-chloro-6-deoxysucrose, 6,6′-dichloro-6,6′-dideoxysucrose, and 6-chloro-6-deoxy-D-glucose were 1.0 (brownish yellow), 1.1 (dark brown), 1.14 (bright lemon-yellow), 1.24 (brownish lemon-yellow), 2.17 (brown), and 1.36 (brown), respectively. The hydrolysate showed the presence of two products which were coincident in R_S values and colours with 6-chloro-6-deoxy-D-glucose and D-fructose, respectively.

6,6′-Dibromo-6,6′-dideoxysucrose hexabenzoate (**11**). — A solution of 6,6′-di-*O*-tosylsucrose hexabenzoate in $(Me_2N)_3PO$ (6.0 ml) containing sodium bromide (2.0 g) was heated for 6 h at 85° with stirring. T.l.c. (ether–light petroleum, 4:1) showed the presence of a major and a minor product that had higher and lower R_F values, respectively, than the starting material. The reaction mixture was worked up in the usual way, and the precipitate formed was taken up in acetone. The acetone solution was dried ($MgSO_4$), filtered, and concentrated. A solution of the syrupy residue in dry pyridine (10 ml) was cooled to 0°, benzoyl chloride (10 ml) was added dropwise over a period of 10 min, and then the reaction mixture was allowed to rise slowly to room temperature. After 16 h, t.l.c. (ether–light petroleum, 4:1) showed a single spot running faster than the starting material. Pyridine was removed by co-distillation with ethanol, and a solution of the semi-crystalline residue in acetone was decolourised with "Hyflo Supercel"–charcoal. The colourless filtrate was concentrated to a syrup which crystallised from hot ethanol to give the dibromide **11** (1.5 g, 87.5%), m.p. 176–178°, $[\alpha]_D^{30}$ +0.3° (*c* 0.33, chloroform) (Found: C, 59.9; H, 4.2; Br, 14.3. $C_{54}H_{44}Br_2O_{15}$ calc.: C, 59.5; H, 4.0; Br, 14.5%). N.m.r. data: τ 3.64 (*d*, 1 proton, $J_{1,2}$ 3.0 Hz, H-1), 4.46 (*q*, 1 proton, $J_{2,3}$ 10.0 Hz, H-2), 4.16 (*t*, 1 proton, $J_{3,4}$ 10.0 Hz, H-3), 4.38 (*t*, 1 proton, $J_{4,5}$ 10.0 Hz, H-4), 3.78 (*d*, 1 proton, $J_{3',4'}$ 7.0 Hz, H-3′), 3.98 (*t*, 1 proton, $J_{4',5'}$ 7.0 Hz, H-4′).

*6-Deoxy-β-*D-xylo*-hex-5-enopyranosyl 6′-deoxy-β-*D-threo*-hex-5′-enofuranoside hexabenzoate.* — A solution of the dibromide **11** (200 mg) in dry pyridine (10 ml) was stirred with anhydrous silver fluoride for 4.5 h, after which time t.l.c. (ether–light petroleum, 6:1) showed one product that was faster running than the starting material. The reaction mixture was poured into ice–water, and the brown precipitate was filtered off, washed well with cold water, and dissolved in acetone. The solution was decolourised with charcoal, dried ($MgSO_4$), and concentrated to a syrup which crystallised from hot methanol to give the 5,5'-diene (100 mg, 52%), m.p. and mixed m.p. 150–151°; lit.[1] m.p. 145–147° (Found: C, 69.1; H, 4.6. $C_{54}H_{42}O_{15}$ calc.: C, 69.4; H, 4.5%).

6,6'-Diazido-6,6'-dideoxysucrose hexa-acetate (**8**). — A solution of the 6,6'-dichloride **2** (500 mg) in $(Me_2N)_3PO$ (3 ml) containing sodium azide (500 mg) was heated for 3 h at 85° with stirring. T.l.c. (ether–light petroleum 4:1) then showed a faster moving product, and a slower moving spot probably due to some de-acetylation. The reaction mixture was worked up in the usual way. A solution of the white precipitate in acetone was dried ($MgSO_4$) and concentrated, the syrupy residue was taken up in pyridine (10 ml), acetic anhydride (6 ml) was added, and the reaction mixture was left at room temperature for 16 h. T.l.c. (ether–light petroleum, 4:1) then showed one major product, and the mixture was poured into ice–water and the syrup formed was extracted with chloroform. The chloroform extract was washed with water, dilute hydrochloric acid, water, saturated aqueous sodium hydrogen carbonate, and water, dried ($MgSO_4$), and concentrated to a syrup. Purification by p.l.c. (ether–light petroleum, 4:1; detection with iodine) gave the diazide **8** as a syrup (400 mg, 84%), $[\alpha]_D^{26}$ +5.8° (*c* 5.4, chloroform) (Found: C, 45.4; H, 5.3; N, 12.7. $C_{24}H_{32}N_6O_{15}$ calc.: C, 44.7; H, 4.9; N, 13.0%). N.m.r. data: τ 4.28 (*d*, 1 proton, $J_{1,2}$ 3.5 Hz, H-1), 5.12 (*q*, 1 proton, $J_{2,3}$ 10.0 Hz, H-2), 4.5 (*q*, 1 proton, $J_{3,4}$ 9.0 Hz, H-3), 4.98 (*t*, 1 proton, $J_{4,5}$ 9.0 Hz, H-4), 4.48 (*d*, 1 proton, $J_{3',4'}$ 6.0 Hz, H-3'), 4.64 (*t*, 1 proton, $J_{4',5'}$ 6.0 Hz, H-4'), 7.8–8.1 (*m*, 18 protons, Ac).

6,6'-diazido-6,6'-dideoxysucrose (**9**). — A solution of **8** (1.0 g) in dry methanol 100 ml) was treated with 2M methanolic sodium methoxide (1 ml) at room temperature for 3 h. T.l.c. (chloroform–ethanol, 5:3) then showed one product running slower than the starting material. After neutralisation with Amberlite IRC-50 (H^+) resin (previously washed with methanol), the solution was concentrated. The syrup residue was boiled with light petroleum which was then decanted carefully, and this operation was repeated three times to remove all of the methyl acetate. The product was dried over phosphoric oxide and paraffin wax overnight to give the diazide **9** as a syrup (520 mg, 80%), $[\alpha]_D$ +62.8° (*c* 1.0, water) (Found: C, 36.3; H, 5.1; N, 20.7. $C_{12}H_{20}N_6O_9$ calc.: C, 36.7; H, 5.1; N, 21.4%). Compound **9** has now been crystallised by Dr. R. Khan (Tate & Lyle, Ltd.) and has m.p. 163–164°, $[\alpha]_D$ +78.8° (*c* 0.98, water).

6-Azido-6-deoxysucrose heptabenzoate (**12**). — A solution of 6-chloro-6-deoxysucrose heptabenzoate[2] (**7**) (100 mg) in $(Me_2N)_3PO$ (3 ml) with sodium azide (100 mg) was heated for 3 h at 85° with stirring. The reaction mixture was poured on to ice–water and worked up, as above, and the syrupy product was crystallised from ethanol to give the 6-azide **12** (90 mg, 89%), m.p. 80–83°, $[\alpha]_D^{29}$ +28.5° (*c* 0.07, acetone) (Found: C, 67.0; H, 4.6; N, 3.3. $C_{61}H_{49}N_3O_{17}$ calc.: C, 66.8; H, 4.5; N, 3.8%).

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REFERENCES

1 Part V: R. Khan, *Carbohyd. Res.*, 25 (1972) 232.
2 C. H. Bolton, L. Hough, and R. Khan, *Carbohyd. Res.*, 21 (1972) 133.
3 E. Reinefeld and S. Klaudianos, *Zucker*, 21 (1968) 330.
4 R. U. Lemieux and A. G. McInnes, *Can. J. Chem.*, 40 (1962) 2394.
5 B. T. Lawton, W. A. Szarek, and J. K. N. Jones. *Carbohyd. Res.*, 15 (1970) 397.
6 P. D. Bragg, J. K. N. Jones, and J. C. Turner, *Can. J. Chem.*, 37 (1959) 2243.
7 B. T. Lawton, W. A. Szarek, and J. K. N. Jones, *Chem. Commun.*, (1969) 787; M. Parolis, W. A. Szarek, and J. K. N. Jones, *Carbohyd. Res.*, 19 (1971) 97.
8 M. E. Evans, L. Long, Jr., and F. M. Parrish, *J. Org. Chem.*, 33 (1968) 1074.
9 A. C. Richardson, *Carbohyd. Res.*, 10 (1969) 395.
10 L. Hough and K. S. Mufti, unpublished results.
11 B. Helferich and H. Bredereck, *Ber.*, 60 (1927) 1995.