NUCLEOPHILIC DISPLACEMENT REACTIONS IN CARBOHYDRATES THE FORMATION OF 1,4-ANHYDRO-6-DEOXY-2,3-O-isopropylidene- β -l-talopyranose (1,5-ANHYDRO-6-DEOXY-2,3-O-isopropylidene- α -l-talofuranose)

J. S. BRIMACOMBE AND L. C. N. TUCKER

Chemistry Department, The University, Birmingham 15 (Great Britain) (Received March 3rd, 1967)

INTRODUCTION

In a recent report¹, we described a base-catalysed rearrangement of 2,3:6,7-di-O-isopropylidene-5-O-methanesulphonyl-D-glycero-D-gulo-heptofuranose, leading to the formation, amongst other products, of 1,4-anhydro-2,3:6,7-di-O-isopropylidene- α -D-glycero-D-allo-heptopyranose, which was considered to arise by an intramolecular, nucleophilic displacement. However, there is some confusion as to the stereochemistry of the products formed by such reactions, and some of the early reports on the formation of 1,4-anhydro sugars are not based on rigorous chemical characterisation and warrant closer scrutiny.

Treatment of 2,3,6-tri-O-methyl- α -D-glucosyl chloride with sodium in ether was reported by Freudenberg and Braun² to yield a 1,4-anhydro compound that was unreactive towards Fehling's solution, bromine water, and potassium permanganate solution. A later attempt³ to reproduce this synthesis apparently yielded only unsaturated products. Micheel and Micheel⁴ examined the action of trimethylamine in ethanol-benzene on 2,3,4-tri-O-acetyl- α -L-rhamnopyranosyl bromide and obtained a crystalline product, which was weakly reducing towards Fehling's solution and was considered to be 2,3-di-O-acetyl-1,4-anhydro- α -L-rhamnopyranose. It was also claimed⁵ that the reaction of 2,3,6-tri-O-methyl-4-O-toluene-p-sulphonyl-D-glucopyranose with sodium methoxide gave 1,4-anhydro-2,3,6-tri-O-methyl- β -L-idopyranose, with inversion occurring at C-5, rather than at the carbon atom bearing the sulphonate group.

The latter reaction was re-investigated by Kops and Schuerch⁶, and it was demonstrated that the anhydro sugar has the D-galacto configuration, and so the displacement follows the expected stereochemical course. Similarly, an unresolved mixture of 2,3-di-O-methyl-4(5)-O-toluene-p-sulphonyl-D-xylopyranose(furanose) afforded 1,4-anhydro-2,3-di-O-methyl- α -L-arabinopyranose and 1,4-anhydro-2,3-di-O-methyl- α -L-arabinopyranose and 1,4-anhydro-2,3-di-O-methyl- α -D-xylopyranose on treatment with sodium isopropoxide⁶.

1,4-Anhydropyranoses may also be regarded⁷ as 1,5-anhydrofuranoses, so that displacement reactions at C-5 of a furanose provide an alternative route to these compounds. Thus, 1-O-acetyl-2,3,6-tri-O-methyl-5-O-toluene-p-sulphonyl-D-gluco-furanose is converted by the action of sodium methoxide into an anhydro sugar, which originally was assigned⁸ the D-gluco configuration, but which, in the light of

present-day knowledge, can be assigned the structure 1,5-anhydro-2,3,6-tri-O-methyl- α -L-idofuranose (1,4-anhydro-2,3,6-tri-O-methyl- β -L-idopyranose). Vis and Fletcher⁷ reported that both 2,3-O-benzylidene- and 2,3-O-isopropylidene-5-O-toluene-p-sulphonyl-D-ribofuranose are converted into the corresponding 1,5-anhydro- β -D-ribofuranoses with sodium isopropoxide.

In view of the controversy over the structures of some of the 1,4-anhydro sugars known at the start of our investigation, particularly those resulting from intramolecular displacements on a pyranoid ring, we have examined the formation of such compounds by using 2,3-O-isopropylidene-4-O-methanesulphonyl-L-rhamnopyranose (3) as a representative molecule. Additionally, it was hoped to gain some information on the rate of formation of 1,4-anhydro sugars, under conditions comparable to those used in our previous investigation¹.

DISCUSSION

A convenient starting-point for the preparation of compound 3 is benzyl α -Lrhamnopyranoside, since subsequent removal of the glycosidic substituent can be accomplished under mild, catalytic conditions⁹. The rhamnopyranoside is isolated¹⁰ only with difficulty from the acid-catalysed reaction of L-rhamnose with benzyl alcohol, but is smoothly converted into benzyl 2,3-O-isopropylidene- α -L-rhamnopyranoside(1) on treatment with acidified acetone. Later, it was found that compound 1 could be isolated, in crystalline form, by acetonation of the original rhamnoside mixture. Reaction of compound 1 with methanesulphonyl chloride in pyridine afforded benzyl 2,3-O-isopropylidene-4-O-methanesulphonyl- α -L-rhamnopyranoside (2). In passing, it is interesting to note that the n.m.r. spectra of compounds 1 and 2 showed that the glycosidic benzyl group has a restricted rotation, since the signals of the methylene protons appear as an AB system (see Experimental); this effect has been observed¹¹ with benzyl ethers of other carbohydrates.



Carbohyd. Res., 5 (1967) 36-44

Catalytic debenzylation of glycoside 2 afforded crystalline 2,3-O-isopropylidene-4-O-methanesulphonyl-L-rhamnopyranose (3), together with a small proportion of a product (4), arising from cleavage of the acetal group. The latter compound exhibited upwards mutarotation indicative of an α -L configuration. In agreement with this assignment. the n.m.r. spectrum (deuterium oxide) initially showed a narrow doublet at τ 4.91, ascribed to the anomeric proton of the α -L form, whilst that of the equilibrium solution exhibited two narrow doublets at τ 4.91 and 5.13. Compound 3 had a positive rotation $(+36^\circ)$ in methanol but did not mutarotate in this or several other solvents. Its n.m.r. spectrum (deuteriochloroform containing some deuterium oxide) revealed the presence of a single anomer that gave rise to a singlet for H-1 at τ 4.67; the spectrum was unchanged after two days, and, in the absence of deuterium oxide. the signal for H-1 appeared as a doublet due to coupling with the hydroxylic proton. The signal for the anomeric proton appeared as a singlet at τ 4.68 when the spectrum was measured in deuterium oxide. but since compound 3 was only sparingly soluble in this solvent, the presence of a small proportion of the other anomer cannot be excluded. Angyal et al.¹² have shown that for an aqueous, equilibrium solution of 2.3-O-isopropylidene-4-O-methyl-L-rhamnopyranose, the H-1 signal for the α -anomer appears as a singlet at τ 4.71 and for the β -anomer as a doublet at τ 4.90; in deuteriochloroform, these signals occur at τ 4.70 and 5.10, respectively. This evidence suggests that compound 3 crystallises as the α -L anomer.

On treatment with sodium methoxide in methanol at room temperature, compound 3 was rapidly (ca. 15 min) converted into a single product with the precipitation of sodium methanesulphonate. The product was obtained as a readily volatile solid, which was best purified by sublimation. It had a molecular weight (mass spectrometry) of 186 and exhibited no infrared absorption attributable to either C=C or OH groups. These data suggested that the product is 1,4-anhydro-6deoxy-2,3-O-isopropylidene- β -L-talopyranose (1,5-anhydro-6-deoxy-2,3-O-isopropylidene- α -L-talofuranose) (5), and this structure is supported unequivocally by n.m.r. spectroscopy and chemical evidence. The n.m.r. spectrum of 5 (Fig. 1) is extremely simple, since no coupling is observed between H-1-H-2, H-3-H-4, H-4-H-5, which subtend dihedral angles of ca. 80° on the bicyclic ring-system, and H-2 and H-3 appear to be equivalent. The quartet at $\tau 6.55$, corresponding to one proton, can clearly be ascribed to H-5. Acid hydrolysis of anhydro sugar 5 proceeded as expected for a 1,4(1,5)-glycosan to yield 6-deoxy-L-talose (chromatographic identification) as the only reducing component. The sugar was characterised as the crystalline phenylosazone (6), which was identical with that prepared from L-fucose.

In view of our present experience and other evidence⁶, it appears that intramolecular displacements of pyranose 4-sulphonates yield products having the expected stereochemistry. However, recent evidence^{13,14} suggests that, in our case, the mechanism may not be as straightforward (see later).

As an alternative, we examined the preparation of anhydro sugar 5 by intramolecular displacement of the sulphonate group of 6-deoxy-2,3-O-isopropylidene-5-O-methanesulphonyl-D-allofuranose (10). On treatment with sodium benzyl oxide in

benzyl alcohol, 2,3-O-isopropylidene-5-O-toluene-p-sulphonyl-L-rhamnofuranose (7) was converted into crystalline benzyl 6-deoxy-2,3-O-isopropylidene- β -D-allofuranoside (8) by a rearrangement analogous to that observed with sodium methoxide¹⁵. Compound 8 gave 6-deoxy-D-allose on acid hydrolysis, and its infrared and n.m.r. spectra (see Experimental) were in complete agreement with the structure assigned;



Fig. 1. The n.m.r. spectrum of 1,4-anhydro-6-deoxy-2,3-O-isopropylidene- β -L-talopyranose (5) in deuteriochloroform at 60 MHz.

the methylene protons of the benzyl group again appeared as an AB system. The derived methanesulphonate (9) was obtained as a syrup that could not be freed entirely from impurities. It is likely that the impurities were responsible for deactivating the palladium-charcoal catalyst used in subsequent, unsuccessful attempts to remove the glycosidic benzyl group. Compound 9 was therefore hydrolysed under conditions to remove both the acetal and glycosidic substituents. The resulting syrup was re-acetonated to give a product that was presumed to be mainly 6-deoxy-2,3-O-isopropylidene-5-O-methanesulphonyl-D-allofuranose (10), since treatment with sodium methoxide rapidly converted it into anhydro sugar 5. The overall yield of anhydro sugar 5 obtained by this sequence was low, and the first procedure is clearly the method of choice.

If the conversion $3\rightarrow 5$ proceeds by a normal, intramolecular displacement, it must involve the β -L anomer, since only in this configuration and by adopting a boat conformation of the pyranoid ring can the molecule attain the correct stereochemistry. There is evidence^{13,14} to indicate that bimolecular, nucleophilic reactions of rhamno-

pyranoside 4-sulphonates occur via an unusual ring-contraction involving participation of the C-5-ring oxygen bond, which is *trans*-antiparallel to the bond undergoing cleavage. An analogous mechanism could presumably operate in the formation of anhydro sugar 5 by an intramolecular displacement and must necessarily occur through the α -L anomer. The rapid deposition of sodium methanesulphonate prevented any measurement of optical rotational changes when the base was added to a solution of compound 3 in methanol. A choice between these possibilities may be possible when the mechanism of displacement reactions of rhamnopyranoside 4-sulphonates is fully established.



The dramatically different reactions of compounds 7 and 10 with base is also worthy of comment*. Two points can be made. With compound 7, anhydro-ring formation would require that the nucleophile approach the sulphonate group from within the V-shape formed by the trioxabicyclo[3.3.0]octane ring-system, where it is likely to experience adverse steric and/or electronic interactions. Secondly, in the transition state for this reaction, a severe, steric interaction will be introduced between the C-5 hydrogen atom and the relatively inflexible 1,3-dioxolan ring. These interactions are presumably sufficient to divert the reaction to another course^{15,21}.

These considerations do not apply in the case of compound 10, and it is significant that, in the transition state for the reaction leading to anhydro sugar 5, the 1,3dioxolan ring is approaching an *exo*-configuration with respect to the bioxabicyclo-[2.2.1]heptane ring-system being formed. The same consideration holds for other 2,3-O-isopropylidenefuranose sulphonates where anhydro-ring formation is observed^{1.7}. The ease of intramolecular, nucleophilic displacement of the sulphonate group in this instance is also of interest in view of a report¹⁴ that displacements with methyl 6-deoxy-2,3-O-isopropylidene-5-O-p-bromobenzenesulphonyl- β -L-allofuranoside involve participation and migration of the methoxyl group.

EXPERIMENTAL

Thin-layer chromatography (t.l.c.) was performed on Kieselgel G and detection was effected with vanillin-sulphuric acid¹⁶. N.m.r. spectra were normally obtained

^{*}We have included this discussion at the suggestion of a referee, to whom we are indebted for valuable comment. A detailed discussion of the effects governing anhydro-ring formation in other molecules is reserved for a later communication.

with a Varian A-60 spectrometer for ca. 10% solutions in deuteriochloroform with tetramethylsilane as internal reference; for solutions in deuterium oxide, sodium 4,4-dimethyl-4-silapentane-1-sulphonate was used as reference. Infrared spectra were recorded for Nujol mulls with a Perkin-Elmer Infracord spectrometer, or for comparative purposes, on ca. 3% solutions in carbon tetrachloride with a Perkin-Elmer 125 spectrometer. Molecular weights were measured on an A.E.I. MS9 mass spectrometer.

Benzyl 2,3-O-isopropylidene- α -L-rhamnopyranoside (1). — L-Rhamnose monohydrate (25 g) was dissolved in redistilled benzyl alcohol (300 ml) containing conc. hydrochloric acid (3 ml), and the solution was stored for 3 days at room temperature and then neutralised with conc. ammonia (2.5 ml). The excess of benzyl alcohol was largely removed under diminished pressure to yield a syrup that contained a major component indistinguishable in its chromatographic behaviour (t.l.c., acetonetoluene, 1:1) from that of authentic benzyl α -L-rhamnopyranoside¹⁰. The syrup was taken up in dry acetone (1 litre) containing conc. sulphuric acid (3 ml) and kept for 1 h at room temperature. After the acid had been neutralised with conc. ammonia (10 ml), the solvents were removed, and the residue was extracted with chloroform (500 ml), which was washed with water (3×500 ml) and dried (MgSO₄). Removal of the chloroform afforded an oil, containing benzyl alcohol, which yielded the product, b.p. 155-165°/0.075 mm, on fractional distillation. The distillate crystallised on standing and gave compound 1 (11 g, 27%), m.p. 73–75°, $[\alpha]_{\rm D}$ – 55° (c 1, chloroform), on recrystallisation from light petroleum (b.p. 80-100°) (Found: C, 65.2; H, 7.2. $C_{16}H_{22}O_5$ calc.: C, 65.3; H, 7.5%). N.m.r. data: τ 2.70 (5-proton singlet, aromatic); 4.98 (singlet, H-1); 5.42 (AB quartet, J 12 Hz, benzyl methylene protons); 8.48, 8.66 (3-proton singlets, CMe₂); 8.70 (3-proton doublet, J_{5,6} 6 Hz, C₍₅₎-Me).

The compound prepared by the above procedure was identical (t.l.c., infrared spectrum, m.p. and mixed m.p.) with that obtained by acetonation of crystalline benzyl α -L-rhamnopyranoside¹⁰ (kindly donated by Dr. M. C. Cock).

Benzyl 2,3-O-isopropylidene-4-O-methanesulphonyl- α -L-rhamnopyranoside (2). — Methanesulphonyl chloride (5 ml) was added to a solution of compound 1 (3 g) in dry pyridine (75 ml), and the mixture was stored for 24 h at room temperature. Water (3 ml) was added and, after 15 min, the solution was added to ether (200 ml), which was washed with water (3 × 200 ml) and dried (MgSO₄). Removal of the solvent, with recrystallisation of the residue from aqueous methanol and finally from ether–light petroleum (b.p. 40–60°), gave compound 2 (3.1 g), m.p. 87–88°, [α]_D – 28° (c 2, methanol). (Found: C, 55.05; H, 6.6; S, 8.4. C₁₇H₂₄O₇S calc.: C, 54.8; H, 6.45; S, 8.6%). N.m.r. data: τ 2.68 (5-proton singlet, aromatic); 4.93 (singlet, H-1); 5.40 (AB quartet, J 12 Hz, benzyl methylene protons); 6.84 (3-proton singlet, MeSO₂); 8.43, 8.65 (3-proton singlets, CMe₂); 8.69 (3-proton doublet, J_{5.6} 6 Hz, C₍₅₎-Me).

2,3-O-Isopropylidene-4-O-methanesulphonyl- α -L-rhamnopyranose (3) and 4-Omethanesulphonyl- α -L-rhamnopyranose (4). — A solution of glycoside 2 (3 g) in methanol (250 ml) containing a suspension of 5% palladium-on-charcoal (1 g) was shaken under a slight overpressure of hydrogen for 7 days, whereupon t.l.c. (acetonetoluene, 1:3) showed the complete disappearance of starting material (R_p 0.6) and the

formation of two products (R_F 0.1 and 0.4). The catalyst was filtered off, and the filtrate was concentrated, under reduced pressure, to a solid residue. Recrystallisation from methanol-ether gave compound 4 (0.36 g), m.p. 142–143° (decomp.), $[\alpha]_D - 13°$ (2 min) $\rightarrow ca. 0°$ (equil) (c 1, water) (Found: C, 34.9; H, 5.8; S, 13.3. $C_7H_{14}O_7S$ calc.: C, 34.7; H, 5.8; S, 13.25%). N.m.r. data for an equilibrated solution in deuterium oxide: τ 4.91, 5.13 (doublets, $J_{1,2}$ ca. 1.5 Hz, 1 proton, anomeric protons); 6.72 (3-proton singlet, MeSO₂); 8.70 (3-proton doublet, $J_{5,6}$ 6 Hz, $C_{(5)}$ -Me). The mother liquors were concentrated, and the residue was recrystallised from ether–light petroleum (b.p. 40–60°) to yield compound 3 (1.4 g), m.p. 91–92°, $[\alpha]_D + 36°$ (c 1, methanol); no mutarotation was observed in chloroform, methanol, or aqueous methanol (Found: C, 42.4; H, 6.2; S, 11.7. $C_{10}H_{18}O_7S$. calc.: C, 42.7; H, 6.4; S, 11.4%). N.m.r. data: τ 4.67 (doublet, J 3 Hz, H-1); 6.86 (3-proton singlet, MeSO₂); 8.43, 8.67 (3-proton singlets, CMe₂); 8.67 (3-proton doublet, $J_{5,6}$ 6 Hz, $C_{(5)}$ -Me); on the addition of deuterium oxide, the signal at τ 4.67 collapsed to a singlet.

Benzyl 6-deoxy-2,3-O-isopropylidene- β -D-allofuranoside (8). — 2,3-O-Isopropylidene-5-O-toluene-p-sulphonyl-L-rhamnofuranose¹⁵ (6 g) was added to a solution of sodium benzyl oxide [250 ml; prepared with sodium hydride (2 g)], and the mixture was stored for 7 days at room temperature. The excess of reagent was destroyed with carbon dioxide, and the mixture was dispersed in water (200 ml), which was extracted with ethyl acetate (2 × 200 ml). Concentration of the dried (MgSO₄) extracts yielded an oil that contained a substantial proportion of benzyl alcohol. This was removed by distillation under diminished pressure (*ca*. 63°/0.1 mm), and further distillation afforded compound **8** (4.5 g), b.p. 115–120°/0.05 mm, as a syrup that crystallised on standing. The alloside **8** was recrystallised, with difficulty, from methanol and had m.p. 66–67°, [α]_D – 101° (*c* 1, chloroform) (Found: C, 65.2, H, 7.4. C₁₆H₂₂O₅ calc.: C, 65.3; H, 7.5%). N.m.r. data: τ 2.67 (5-proton singlet, aromatic); 4.82 (singlet, H-1); 5.32 (AB quartet, J 12 Hz, benzyl methylene protons); 8.52, 8.68 (3-proton singlets, CMe₂); 8.78 (3-proton doublet, $J_{5,6}$ 7 Hz, C₍₅₎-Me).

Hydrolysis of alloside 8 (40 mg) in boiling dioxane (1 ml) with 2N sulphuric acid (1 ml) for 4 h gave, after neutralisation and concentration, 6-deoxy-D-allose, m.p. and mixed m.p. $144-145^{\circ}$ (lit.¹⁵, m.p. 151-152°).

Benzyl 6-deoxy-2,3-O-isopropylidene-5-O-methanesulphonyl- β -D-allofuranoside (9). — Compound 8 (0.1 g) in a mixture of chloroform (5 ml) and pyridine (5 ml) was treated at room temperature with methanesulphonyl chloride (0.2 ml) for 12 h, and the solution was then processed in the usual manner. The sulphonate (9) (0.14 g), $[\alpha]_D$ — 80° (c 1, chloroform), was obtained as a chromatographically homogeneous syrup, which could not be induced to crystallise and was contaminated with solvent.

6-Deoxy-2,3-O-isopropylidene-5-O-methanesulphonyl-D-allofuranose (10). — Attempts to remove the glycosidic benzyl substituent by catalytic means were unsuccessful, and the following procedure was adopted.

The sulphonate 9 (0.14 g) in acetone (5 ml) was heated under reflux with N hydrochloric acid (5 ml) for 30 min, whereafter the hydrolysate was diluted with water (100 ml), extracted with ether (2 \times 50 ml), and neutralised with Amberlite IRA-400

 (CO_3^{2-}) . The solvents were removed to give a syrup (68 mg), which appeared to be homogeneous by t.l.c. (toluene-acetone, 3:1). The syrup was acetonated with acidified acetone in the normal way to yield a slightly impure, syrupy product (73 mg), $[\alpha]_D + 3^\circ$ (c 2, ether). The syrup appeared to be essentially homogeneous by t.l.c., whilst n.m.r. spectroscopy demonstrated the presence of both sulphonate and acetal substituents, but also indicated the presence of contaminants, which were not readily removed.

1,4-Anhydro-6-deoxy-2,3-O-isopropylidene- β -L-talopyranose (5). — (a) 2,3-O-Isopropylidene-4-O-methanesulphonyl-L-rhamnopyranose (0.5 g) was treated with N sodium methoxide in methanol (5 ml) for 1 h at room temperature; t.l.c. showed that the reaction was essentially complete after 15 min. The reaction mixture was dispersed in ether (200 ml) and washed successively with dilute sulphuric acid (200 ml) and water (200 ml). Concentration of the dried (MgSO₄) organic layer yielded a crystalline residue (0.27 g), which was sublimed (ca. 70°/15 mm) to give anhydro sugar 5 (0.21 g, 60%), m.p. 71–73°, $[\alpha]_D -51°$ (c 1, methanol) (Found: C, 58.4; H, 7.65. $C_9H_{14}O_4$ calc.: C, 58.1; H, 7.5%). The mass spectrum of the product contained a top mass peak at 171 (M-15) corresponding¹⁷ to a molecular weight of 186. Subsequent experience indicated that considerable loss of material occurred during evaporation of the ether solution.

Hydrolysis of the anhydro sugar (0.15 g) in dioxane (1 ml) was accomplished with 2N sulphuric acid (1 ml) in a sealed tube for 2 h at 90–100°. After neutralization with Amberlite IRA-400 (CO_3^{2-}), the solution was concentrated to yield a syrupy, reducing sugar (80 mg) with chromatographic properties indistinguishable from those of 6-deoxy-L-talose. The osazone (6), prepared in the usual manner¹⁸, had m.p. 168–170° (from aqueous ethanol), which was not depressed on admixture with the osazone prepared from L-fucose. Reist *et al.*¹⁹ reported m.p. 168–171° for this derivative, whilst Votoček and Červaný²⁰ gave m.p. 177–178°. The infrared spectra of the osazones were identical.

(b) 6-Deoxy-2,3-O-isopropylidene-5-O-methanesulphonyl-D-allofuranose (73 mg) was treated with N sodium methoxide in methanol (0.5 ml), as described above, to give anhydro sugar 5 (14 mg), m.p. and mixed m.p. 71-73°, on sublimation; t.l.c. showed that only one product was formed. The infrared spectrum and chromatographic properties of the anhydro sugar were indistinguishable from those of previously prepared 5.

ACKNOWLEDGMENTS

The authors thank Professor M. Stacey, C.B.E., F.R.S., for his interest, Dr. E. F. Mooney for measuring some of the n.m.r. spectra, and Dr. J. R. Majer for mass measurements. The award of a maintenance grant (to L.C.N.T.) by Albright and Wilson (Mfg.) Ltd. is gratefully acknowledged.

SUMMARY

The action of sodium methoxide in methanol on 2,3-O-isopropylidene-4-Omethanesulphonyl-L-rhamnopyranose rapidly yields 1,4-anhydro-6-deoxy-2,3-Oisopropylidene- β -L-talopyranose (1,5-anhydro-6-deoxy-2,3-O-isopropylidene- α -L-talofuranose) as the sole product. The structure is assigned on the basis of chemical and n.m.r. evidence. The anhydro sugar is also obtained by similar treatment of 6-deoxy-2,3-O-isopropylidene-5-O-methanesulphonyl-D-allofuranose, prepared from benzyl 6-deoxy-2,3-O-isopropylidene- β -D-allofuranoside.

REFERENCES

- 1 J. S. BRIMACOMBE AND L. C. N. TUCKER, Chem. Commun., (1966) 903.
- 2 K. FREUDENBERG AND E. BRAUN, Ann., 460 (1928) 288.
- 3 K. HESS AND O. LITTMANN, Ber., 66 (1933) 774.
- 4 F. MICHEEL AND H. MICHEEL, Ber., 63 (1930) 2861.
- 5 K. HESS AND F. NEUMANN, Ber., 68 (1935) 1360.
- 6 J. KOPS AND C. SCHUERCH, J. Org. Chem., 30 (1965) 3951.
- 7 E. VIS AND H. G. FLETCHER, JR., J. Am. Chem. Soc., 79 (1957) 1182.
- 8 K. HESS AND K. E. HEUMANN, Ber., 72 (1939) 137.
- 9 C. M. MCCLOSKEY, Advan. Carbohydrate Chem., 12 (1957) 137.
- 10 J. S. BRIMACOMBE, M. C. COOK, AND L. C. N. TUCKER, J. Chem. Soc., (1965) 2292.
- 11 E. G. GROS, Carbohyd. Res., 2 (1966) 56; J. S. BRIMACOMBE AND A. HUSAIN, J. Chem. Soc., in press.
- 12 S. J. ANGYAL, V. A. PICKLES, AND R. AHLUWALIA, Carbohyd. Res., 3 (1967) 300.
- 13 S. HANESSIAN, Chem. Commun., (1966) 796; J. M. WEBBER, personal communication.
- 14 C. L. STEVENS, R. P. GLINSKI, K. G. TAYLOR, P. BLUMBERGS, AND F. SIROKMAN, J. Am. Chem. Soc., 88 (1966) 2073.
- 15 P. A. LEVENE AND J. COMPTON, J. Biol. Chem., 116 (1936) 169.
- 16 Chromatography, E. Merck AG., Darmstadt, 2nd edn., p. 30.
- 17 D. C. DE JONGH AND K. BIEMANN, J. Am. Chem. Soc., 86 (1964) 67.
- 18 L. GATTERMANN, Laboratory Methods of Organic Chemistry, MacMillan, London, 1957, p. 298.
- 19 E. J. REIST, L. GOODMAN, AND B. R. BAKER, J. Am. Chem. Soc., 80 (1958) 5775.
- 20 E. VOTOČEK AND J. ČERVANÝ, Ber., 48 (1915) 658.
- 21 E. J. REIST, L. GOODMAN, R. R. SPENCER, AND B. R. BAKER, J. Am. Chem. Soc., 80 (1958) 3962.