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The mechanism of the hydroxyl → halogen exchange reaction in the presence of triphenylphosphine, *N*-bromosuccinimide, and *N*,*N*-dimethylformamide: application of a new Vilsmeier-type reagent in carbohydrate chemistry

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ABSTRACT

Triphenylphosphine reacts with *N*-bromosuccinimide to give a phosphonium salt (**13**), which reacts with *N*,*N*-dimethylformamide to afford *N*,*N*-dimethylsuccinimidomethaniminium bromide (**16**). The latter product reacts with an alcohol to give an *O*-formiminium compound **17**, and, in the presence of an alcohol, **13** is transformed into an alkoxyphosphonium intermediate (**14**). Both **14** and **17** can be converted by heating into an alkyl bromide. Hydrolysis of **17** gives the corresponding *O*-formyl derivative. Reaction of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose with **13** or **16** gave 6-bromo-6-deoxy-1,2:3,5-di-*O*-isopropylidene-α-D-glucofuranose and a possible mechanism for these reactions is suggested. An efficient method for the preparation of 3-deoxy-3-halogeno-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose derivatives and a new procedure for selective *O*-formylation are described.

INTRODUCTION

For the synthesis of potential inhibitors of HMG-CoA reductase[1], 3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranose (**1**) was needed in large quantities. All syntheses of **1** described so far[2–8] start from 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**2**) and differ only in the methods by which O-3 is removed. For practical reasons, those methods in which **2** is converted into the 3-deoxy-3-iodo-D-*allo* derivative (**4**) followed by reduction[1–3] are preferred. The 3-bromo-3-deoxy (**5**) and 3-chloro-3-deoxy (**6**) derivatives are also suitable intermediates, but, whereas **4** can be obtained in fairly high yield[9–11], only modest yields[12,15] of **5** and **6** have been obtained. Under most reaction conditions[14–24], a rearrangement was observed to afford the corresponding 6-deoxy-6-halogeno-D-*gluco* derivatives **7**–**9**. In seeking a practical synthesis of **5**, the mechanism of this rearrangement has been studied in detail.

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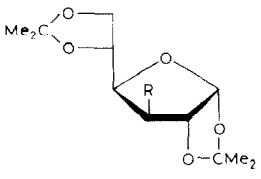
Garegg and Samuelsson[11] converted **2** into the 3-deoxy-3-iodo derivative **4**, using triphenylphosphine, iodine, and imidazole in boiling toluene, whereas Hanessian et al.[23] obtained the 6-bromo-6-deoxy derivative **8** when **2** was treated with *N*-bromosuccinimide and triphenylphosphine in *N*,*N*-dimethylformamide at 50°. When the latter procedure was repeated by Kunz and Schmidt[13] at 40°, only the 3-*O*-formyl-D-*gluco* derivative **3** was formed (52%) and it was necessary to raise the temperature to 100° in order to obtain **8**. It was suggested[13] that an alkoxyphosphonium intermediate **10** was formed first, which reacted at 40° with *N*,*N*-dimethylformamide to form a dialkoxyphosphonium intermediate **11**. Elimination of triphenylphosphine oxide from **11** afforded an iminium salt **12** that yielded the 3-*O*-formyl derivative **3** on quenching with water. However, at 100°, a rearrangement of **10** or **12** occurred and afforded the 6-bromo-6-deoxy derivative **8**. In order to verify this proposed mechanism and to prove whether **8** is formed from **10** or **12**, the reaction has been investigated by NMR spectroscopy.



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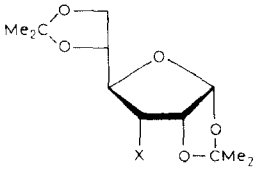
2 R = OH
3 R = OCHO
4 0R = OAc



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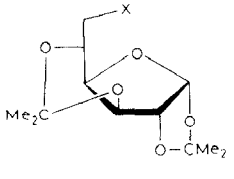
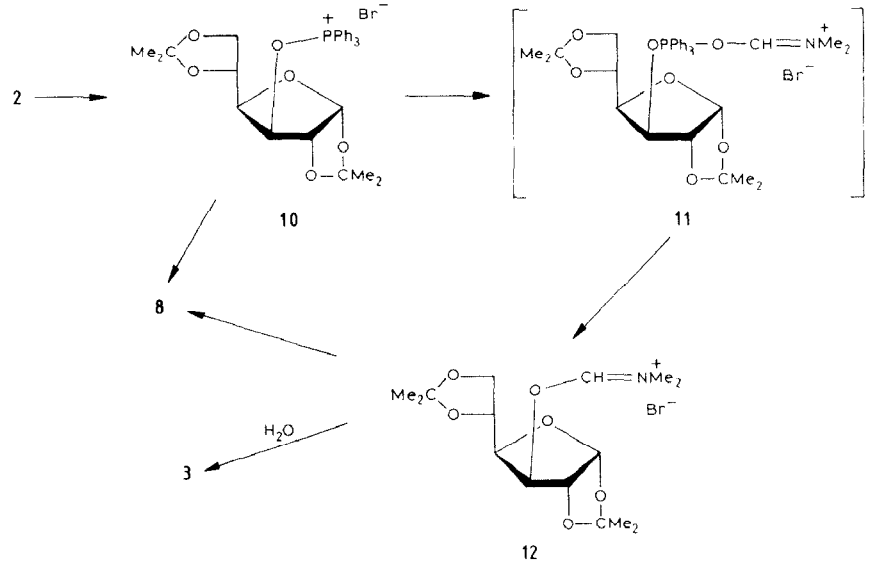
6 X = Cl



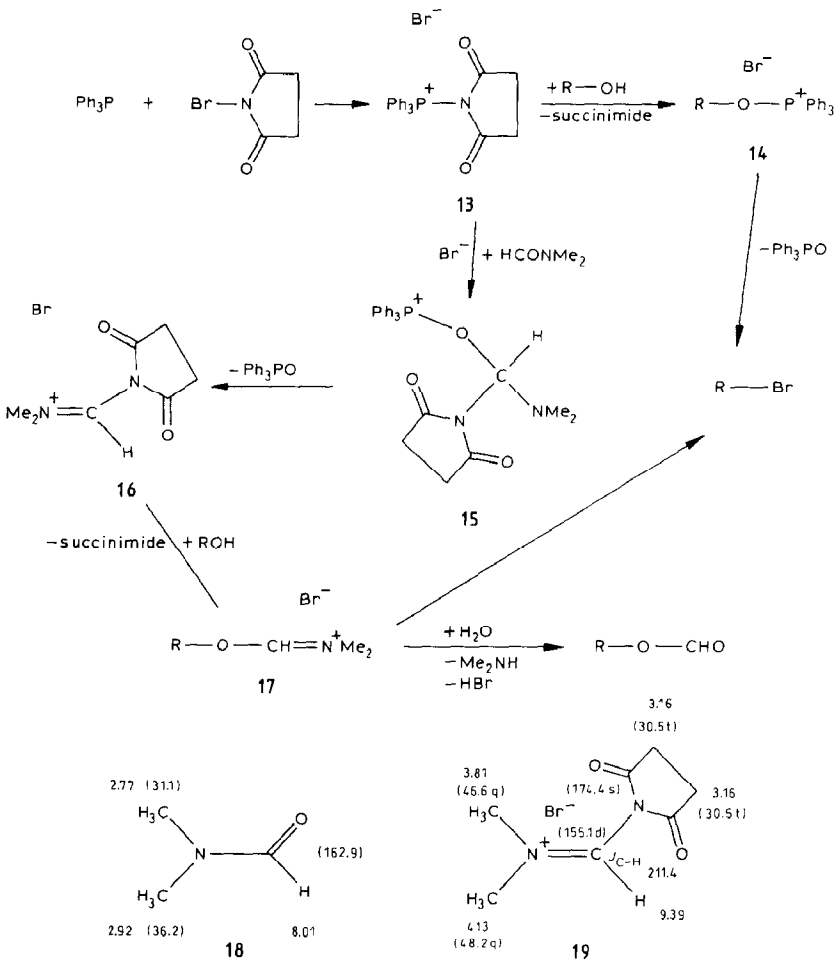
7 X = I
8 X = Br
9 X = Cl



RESULTS AND DISCUSSION

The reaction of alcohols with N-*bromosuccinimide and triphenylphosphine in* N,N-*dimethylformamide.*—The reaction in an NMR tube was monitored by ^{1}H- and ^{13}C-NMR spectroscopy, and the structures of all the intermediates and products were determined. The corresponding phosphonium salt **13** was formed almost instantaneously at 0° and reacted rapidly (~ 2 min at 0°) with *N*,*N*-dimethylformamide to give the formamidinium salt **16** and triphenylphosphine oxide. For comparison, the ^{1}H- and ^{13}C-NMR data of **16** and those of *N*,*N*-dimethylformamide are shown in **19** and **18**.

In order to investigate the reactivities of the phosphonium-type (**14**)[17,19,24] and iminium-type (**17**)[25,26] intermediates, 1,2 : 3,4-di-*O*-isopropylidene-α-D-galactopyranose (**20**) was used as the alcohol. When **20** was added to the amidinium salt **16**, the iminium salt **23** was formed instantaneously, the structure of which was



established by the ^{1}H- (Table I) and ^{13}C-NMR data (Table II). The chemical shift (61.5 ppm) of the C-6 resonance of **20** is increased to 77.3 ppm in **23** due to the iminium group. When water was added to this mixture, the corresponding 6-*O*-formyl derivative **24** (δ 67.7 for C-6) was formed. On heating the solution of **23**, the 6-bromo-6-deoxy derivative **22** (δ 31.8 for C-6) was formed. When the addition of the components was reversed, i.e., **20** was dissolved in *N*,*N*-dimethylformamide, and *N*-bromosuccinimide and triphenylphosphine were added, the reaction followed the mechanism suggested first by Rydon[24], i.e., the alkoxyphosphonium salt **21** was formed (δ 71.3 for C-6) (for NMR data, see Tables I and II). On heating the solution, **21** was converted into the 6-bromo-6-deoxy derivative[23] **22** (δ 31.8 for C-6). The $t_{1/2}$ values of **21** and **23** at 70° were 40 and 120 min, respectively; consequently, the phosphonium group in **21** is a better leaving group than the iminium group in **23**.

Thus, in the case of **2**, depending on the sequence of the addition of the reagents, either the iminium intermediate **12** or the phosphonium intermediate **10** should be formed. Independent of the sequence, the mixture had to be heated to 100° to yield the 6-bromo-6-deoxy derivative **8**. When the mixture was quenched with water before heating to 100°, only the 3-*O*-formyl derivative **3** could be detected; consequently, the iminium salt **12**, and not the phosphonium salt **10**, must have been present as an intermediate. However, when the phosphonium salt **10**[13] was dissolved in *N*,*N*-dimethylformamide, it remained unchanged on heating to 120° and no reaction took place when the amidinium salt **16** was added. Thus, **10** was ruled out as a possible intermediate.

A further possibility was the rearrangement of **2** into 1,2:3,5-di-*O*-isopropylidene-α-D-glucofuranose (**25**) before or during the reaction. Compound **25** is well known[27–32], but no data have been published for its stability and on the rearrangement reaction of **2** and **25**. Conformer **25** was synthesised by the protection of HO-6 of 1,2-*O*-isopropylidene-α-D-glucofuranose (**29**) by silylation ($\rightarrow$ **30**), acid-catalysed reaction with 2-methoxypropene in acetone ($\rightarrow$ **31**), and treatment with tetrabutylammonium fluoride in tetrahydrofuran to afford **25**. The isomerisation of **25** into **2** in *N*,*N*-dimethylformamide catalysed by *p*-toluenesulfonic acid was monitored by NMR spectroscopy, and the results are depicted in Fig. 1. Isomerisation and hydrolysis occurred and, after 3.5 h at 45°, a mixture of **2** (59%), **25** (2%), and **29** (39%) was obtained. A similar mixture resulted after 6 h at 45° when **2** was the starting material. Thus, some **25** will always be formed in a solution of **2** in *N*,*N*-dimethylformamide when an acid is present. As the primary hydroxyl group of **25** reacts more rapidly than the secondary hydroxyl group of **2**, the **2** $\rightleftharpoons$ **25** equilibrium might be shifted towards **25** during the reaction, yielding the 6-bromo-6-deoxy derivative **8** via activation of HO-6.

When *N*-bromosuccinimide and triphenylphosphine were added to a solution of **25** in *N*,*N*-dimethylformamide, the 6-*O*-phosphonium salt **28** was formed as an intermediate. On the other hand, when **25** was added after the reagents, the preformed **16** reacted with **25** to yield the 6-*O*-iminium salt **27**. Both the intermedi-

TABLE 1

^{1}H-NMR data for solutions of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose derivatives in *N*,*N*-dimethylformamide

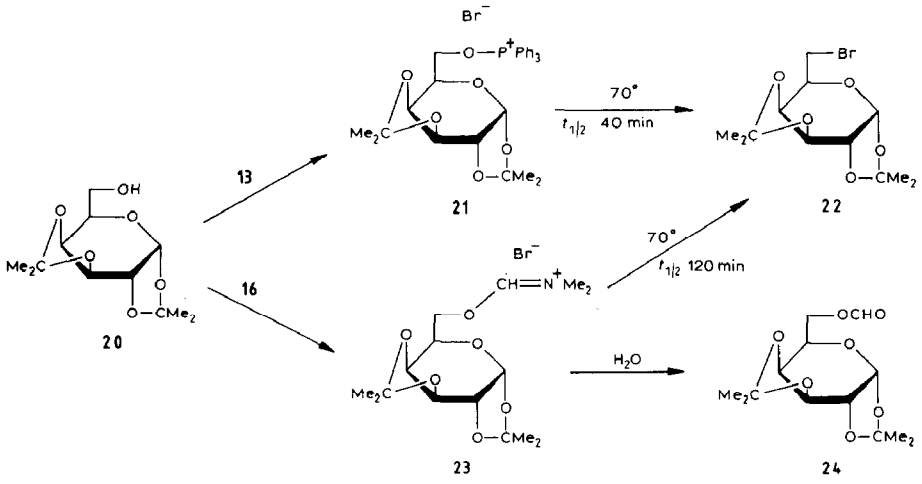
Compound	Chemical shifts (δ)								
	H-1	H-2	H-3	H-4	H-5	H-6a	H-6b	$=CMe_2$	Others
20	5.50	4.36	4.63	4.33	3.86	3.64	3.64	1.47, 1.36, 1.31, 1.31	4.71 (OH)
21	5.48	4.50–4.30	4.70		4.50–4.30			1.54, 1.34, 1.24, 1.26	7.98–7.82, 7.78–7.55 (Ph)
22	5.55	4.43	4.71	4.42	4.00	3.69	3.44	1.48, 1.39, 1.33, 1.33	
23	5.55	4.43	4.69	4.50	4.30	5.12	4.85	1.51, 1.41, 1.33, 1.33	9.82 (=CH), 3.57–3.29 (NMe_2)
24	5.51	4.41	4.67	4.33	4.04	4.24	4.24	1.45, 1.37, 1.31, 1.31	8.28 (=CH)
	Coupling constants (Hz)								
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$J_{6a,6b}$		
20	5.0	2.2	7.9	1.6					
21	5.0	2.4	7.8						
22	4.9	2.3	7.9	1.6	5.0	8.0	10.3		
23	5.0	2.4	7.9	2.0	3.3	7.8	11.3		
24	5.0	2.1	7.9	1.6					

TABLE II

^{13}C-NMR data for solutions of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose derivatives in *N*,*N*-dimethylformamide

Compound	Chemical shifts (δ)								
	C-1	C-2	C-3	C-4	C-5	C-6	Me_2C	CH_3	Others
20	97.0	71.5 [a]	71.4 [a]	71.3 [a]	69.4	61.5	109.1, 108.7	26.4, 26.3, 25.2, 24.6	
21	96.7	71.0 [a]	70.9 [a]	67.8 [a]	67.7 [a]	71.3	109.8, 109.3	26.2, 26.1, 25.2, 24.7	Ph_3P: 120.2 (107.5) [b] (C-1), 130.9 (13.6) [b] (C-2), 134.5 (12.0) [b] (C-3), 136.9 (1.3) [b] (C-4)
22	97.1	71.9 [a]	71.5 [a]	71.1 [a]	69.3	31.8	109.7, 109.1	26.3, 26.3, 25.2, 24.6,	
23	96.7	71.3 [a]	71.2 [a]	70.8 [a]	67.1	77.3	109.9, 109.3	26.3, 26.2, 25.2, 24.6	168.3 (=CH), 41.5, 36.3 (2 NMe)
24	97.0	71.6	71.4	71.1	66.7	63.7	109.8, 109.1	26.3, 26.3, 25.2, 24.6	162.6 (=CH)

[a] Arbitrary assignment. [b] $J_{C,P}$ values (Hz) in brackets.



ates **27** and **28** were converted by heating into the 6-bromo-6-deoxy derivative **8**. As for the galactose derivatives **21** and **23**, the phosphonium salt **28** was more active than the iminium salt **27**, since it was converted into **8** in 50 min at 50°, whereas **27** required 90 min at 70°.

Thus, two conclusions can be drawn. (*a*) The conversion of **2** into **8**, described by Hanessian et al.[23], which could not be reproduced by Kunz et al.[13] or in our studies, must have involved the 6-*O*-phosphonium intermediate **28** since only this product rearranges into **8** at 50°. However, **28** can be formed only from **25**; consequently, the **2** ⇋ **25** rearrangement should be a faster process than the reaction of **2** with the amidinium salt **16** to yield **12**. Since, according to our

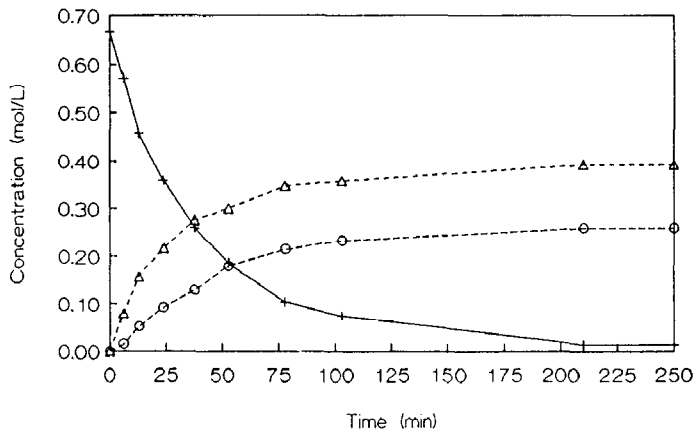
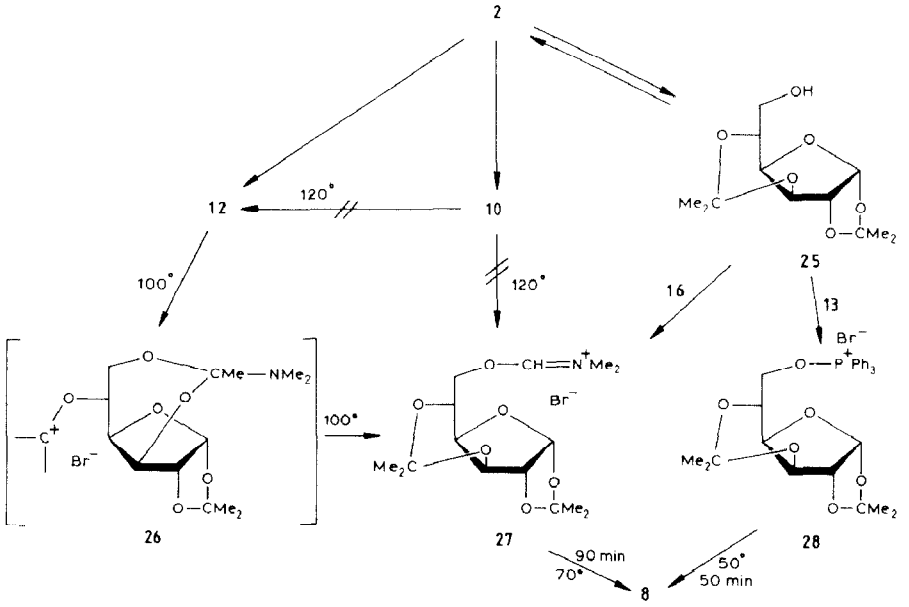


Fig. 1. Isomerisation of 1,2:3,5-di-*O*-isopropylidene-α-D-glucofuranose (**25**, +) in *N*,*N*-dimethylformamide at 45° in the presence of *p*TsOH: △, 1,2:5,6-di-*O*-isopropylidene derivative (**2**); ○, 1,2-*O*-isopropylidene derivative (**29**).

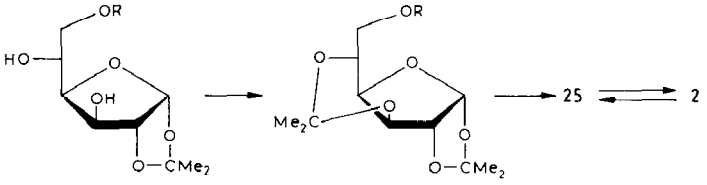


experience, the rearrangement is a much slower process, the reaction temperature given in the literature[23] cannot be correct.

(*b*) Since no bromide **8** was formed below 100°, both the 6-*O*-phosphonium salt **28** and the 6-*O*-iminium compound **27** can be ruled out as intermediates, since they would be converted into **8** at 50° and 70°, respectively. Thus, only the 3-*O*-iminium salt **12** can be the initial intermediate. The rearrangement of **12** into the 6-*O*-iminium salt **27** possibly involves the isopropoxonium cation **26**, the formation of which might be the highest energy-demanding process. As mentioned above, once formed, **27** can be converted at 70° into **8**; consequently, higher energy (100°) is indeed needed for the rearrangement of **12** into **27**.

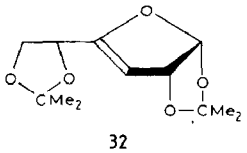
Reaction of alcohols with triphenylphosphine, iodine and imidazole in toluene or chlorobenzene.—In seeking to extend the method of Garegg and Samuelsson[11], who converted **2** into the 3-deoxy-3-iodo derivative **4** (68%) by using triphenylphosphine, iodine, and imidazole in boiling toluene, bromine was used instead of iodine, but the 3-bromo-3-deoxy (**5**) and the 6-bromo-6-deoxy (**8**) derivatives were formed in the ratio 1:1. The role of the dipolar aprotic solvent was demonstrated when the same reagents converted **2** exclusively into the corresponding 6-deoxy-6-halogeno derivatives **7** and **8**, respectively, when *N*,*N*-dimethylformamide was used as the solvent. This result might be due to better solvation of the ionic intermediates, thereby promoting the 5,6 → 3,5 migration of the isopropylidene group. This migration is proton catalysed and it is not surprising that, when *N*-bromosuccinimide was applied in toluene as the brominating reagent, only the 6-bromo-6-deoxy derivative **8** was formed. This result might be due to the fact that the succinimide formed is a more effective catalyst (pK_a 9.7) than imidazole (pK_b 7.0).

Theoretically, a stronger base should prevent the **2** → **25** isomerisation, but, when triphenylphosphine and *N*-bromosuccinimide were used in pyridine, the reaction was extremely slow (~ 8% conversion after boiling for 60 h) since the complex formed is rather insoluble in pyridine. Similar solubility problems prohibited the use of the $[Ph_3P^+\text{-}CX_3]X^-$ (X = Cl, Br, or I) reagent[30] in pyridine. However, triphenylphosphine and *N*-iodosuccinimide in toluene converted **2** into the 3-deoxy-3-iodo derivative **4** (68%) in the presence of imidazole. Toluene could be replaced by chlorobenzene, and each *N*-halogenosuccinimide, in the presence of imidazole at 130°, gave the corresponding 3-deoxy-3-halogeno derivative (**4–6**). The solubility of the different ionic complexes, especially that of the succinimide phosphonium bromide **13** formed initially, is very low in toluene or chlorobenzene. However, precipitation could be avoided if, to a boiling solution of **2**, triphenylphosphine, and imidazole in toluene or chlorobenzene, a solution of iodine in toluene or solid *N*-bromo- or *N*-chloro-succinimide was added slowly. Under these conditions, the phosphonium salts formed react comparatively rapidly, and their concentrations remain below their solubility limits. Thus, **4–6** could be obtained in yields of 87, 66, and 55%, respectively (cf. the highest published [12] yields of 84, 42, and 22%, respectively, using the 3-triflate as leaving group, however, the 3-ene derivative **32** was formed as the major product in addition to **5**

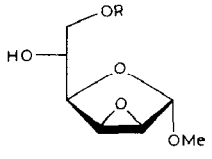


29 R = H
30 R = ^{t}BuMe$_2$Si
34 R = CHO

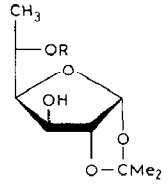
31 R = ^{t}BuMe$_2$Si



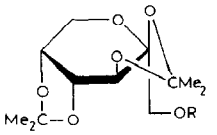
32



33 R = H
36 R = CHO



35 R = H
37 R = CHO



38 R = H
39 R = CHO

and **6**). When the reaction of **2** with triphenylphosphine and *N*-bromo- or *N*-chlorosuccinimide was carried out in chlorobenzene at 130° in the presence of imidazole, only 5–10% of **32** was formed and the corresponding 6-chloro-6-deoxy and 6-bromo-6-deoxy derivatives (**9** and **8**) were formed. The fairly high yields of **4–6** are remarkable since S_N2 reactions of exo-oriented groups attached to *cis*-fused five-membered rings are sterically hindered[33]. The decreasing yields for the different halogens are in good agreement with the known order of reactivity[34,35] $I^- > Br^- > Cl^-$.

Formylation reactions.—The mechanism established above enabled the reaction to be used for the synthesis of partially formylated carbohydrate derivatives. When triphenylphosphine is added at 0° to a solution of *N*-bromosuccinimide in *N*,*N*-dimethylformamide, the formamidinium salt (**16**) is formed immediately. The carbohydrate derivative to be formylated is then added, and the resulting *O*-iminium-type intermediate **17** is quenched by addition of water or aqueous sodium hydrogencarbonate. The advantage of this method over those described[21,25,26] is the absence of phosgene. Moreover, the reaction can be used also in the presence of acid-labile groups, whereas the other known formylation method[36] uses 99% formic acid. The formylations of **29**, **33**, and **35** were regioselective and the corresponding *O*-formyl derivatives **34**, **36**, and **37** were obtained in yields of > 70%, as was that of **39** from **38**. When *N*,*N*-dimethylacetamide was used instead of *N*,*N*-dimethylformamide, the 3-acetate **40** was obtained from **2**. *N*-Chloro- or *N*-iodo-succinimide could be used instead of *N*-bromosuccinimide with similar results.

EXPERIMENTAL

General methods.—Organic solutions were dried over $MgSO_4$ and concentrated under diminished pressure. Optical rotations were determined on 1% solutions in $CHCl_3$ at 20° unless stated otherwise. Solutions were cooled in ice, unless stated otherwise. TLC was performed on Kieselgel G with EtOAc (*A*) and EtOAc–hexane mixtures (*B*, 3:1; *C*, 2:1; *D*, 1:1; *E*, 1:2; *F*, 1:3; *G*, 1:4; and *H*, 1:5) with detection by charring with H_2SO_4. NMR spectra (^1H, 250 MHz; ^{13}C, 75 MHz) were recorded with a Bruker Ac 250 spectrometer on solutions in $CDCl_3$ (internal Me_4Si) unless stated otherwise. Multiplicities of ^{13}C signals were obtained from DEPT experiments.

3-O-Formyl-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (**3**).—Triphenylphosphine (1.51 g) was added in small portions to a cooled and stirred solution of **2** (1.00 g) followed by a solution of *N*-bromosuccinimide (1.03 g) in *N*,*N*-dimethylformamide (25 mL). After 10 min, the temperature was raised to 20° and, after 4.5 h, aq 5% $NaHCO_3$ (2 mL) was added and the mixture was concentrated. A solution of the semicrystalline residue in Et_2O was washed with aq 5% $NaHCO_3$, dried, and concentrated. The residue was extracted with Et_2O, filtered from Ph_3PO, and concentrated. Column chromatography (solvent *E*) of the residue gave **3** (0.75 g, 68%), isolated as a syrup, R_F 0.65 (solvent *D*), $[\alpha]_D^{20}$ −39°; lit.[13]

$[\alpha]_D^{22}$ −36.1°. NMR data: ^{1}H, δ 8.10 (s, 1 H, CHO), 5.89 (d, 1 H, H-1), 5.36 (d, 1 H, H-3), 4.53 (d, 1 H, H-2), 4.25–4.0 (m, 4 H, H-4,5,6a,6b), 1.53, 1.42, 1.33 and 1.32 (4 s, each 3 H, 2 CMe_2); $J_{1,2}$ 3.7, $J_{3,4}$ 1.9 Hz. ^{13}C, δ 159.5 (d, CHO), 112.4, 109.4 (2 s, CMe_2), 105.0 (d, C-1), 83.1, 79.6, 75.7, 72.2 (4 d, C-2,3,4,5), 67.3 (t, C-6), 26.8, 26.6, 26.1, and 25.1 (4 q, 4 CH_3).

3-Deoxy-3-iodo-1,2:5,6-di-O-*isopropylidene-α*-D-allo-*furanose* (**4**).—The original procedure[11] was modified as follows. A solution of I_2 (0.97 g) in toluene (15 mL) was added in small portions during 6 h to a boiling (under reflux), well-stirred solution of **2** (0.5 g), Ph_3P (0.76 g), and imidazole (0.26 g) in toluene (35 mL). Boiling under reflux was then continued for 3 h. The mixture was cooled, toluene (50 mL) and ice (50 g) were added, and the organic phase was washed with cold satd aq $Na_2S_2O_3$, dried, and concentrated. The semicrystalline residue was extracted with Et_2O, the partially crystallised Ph_3PO was removed, and the filtrate was concentrated. Column chromatography (solvent *E*) of the residue gave **4** (0.62 g, 87.3%), mp 54–55° (from hexane), $[\alpha]_D^{20}$ +64°, R_F 0.65 (solvent *D*); lit.[9] mp 55°, $[\alpha]_D^{22}$ +66.3°. The ^{1}H- and ^{13}C-NMR data were in agreement with those published[9,10,12,13].

3-Bromo-3-deoxy-1,2:5,6-di-O-*isopropylidene-α*-D-allo-*furanose* (**5**).—*N*-Bromosuccinimide (0.75 g) was added in small portions during 7 h to a boiling (under reflux) solution of **2** (0.5 g), Ph_3P (0.91 g), and imidazole (0.29 g) in chlorobenzene (40 mL). Boiling under reflux was then continued for 3 h. The mixture was cooled, $CHCl_3$ (50 mL) was added, and the mixture was washed with aq 5% $NaHCO_3$, then processed as described for **4**. Column chromatography (solvent *E*) of the product gave **5** (0.41 g, 66.1%), isolated as a syrup, $[\alpha]_D^{20}$ +52°, R_F 0.65 (solvent *D*); lit.[13] $[\alpha]_D^{22}$ +55°. NMR data: ^{1}H, δ 5.75 (d, 1 H, H-1), 4.61 (dd, 1 H, H-2), 4.30 (td, 1 H, H-5), 4.16 (dd, 1 H, H-4), 4.07 (dd, 1 H, H-6a), 4.00 (dd, 1 H, H-6b), 3.83 (dd, 1 H, H-3), 1.52, 1.42, 1.32, and 1.31 (4 s, each 3 H, 2 CMe_2); $J_{1,2}$ 3.6, $J_{2,3}$ 4.5, $J_{3,4}$ 9.6, $J_{4,5}$ 3.4, $J_{5,6a}$ 6.8, $J_{5,6b}$ 6.8, $^2J_{6a,6b}$ 8.5 Hz.

The fraction having R_F 0.75 (solvent *D*) gave, on concentration, 6-bromo-6-deoxy-1,2:3,5-di-*O*-isopropylidene-*α*-D-glucofuranose (**8**; 0.03 g, 4.8%), isolated as a syrup, $[\alpha]_D^{20}$ +30°, R_F 0.75 (solvent *D*); lit.[13] $[\alpha]_D^{22}$ +30.5°; lit.[23] $[\alpha]_D^{20}$ +19.2°. NMR data: ^{1}H, δ 5.99 (d, 1 H, H-1), 4.59 (d, 1 H, H-2), 4.33 (dd, 1 H, H-4), 4.24 (d, 1 H, H-3), 3.74 (td, 1 H, H-5), 3.62 (dd, 1 H, H-6a), 3.44 (dd, 1 H, H-6b), 1.50, 1.39, 1.37, and 1.33 (4 s, each 3 H, 2 CMe_2); $J_{1,2}$ 3.6, $J_{3,4}$ 3.9, $J_{4,5}$ 7.2, $J_{5,6a}$ 3.2, $J_{5,6b}$ 7.5, $J_{6a,6b}$ 10.9 Hz.

The fraction having R_F 0.7 (solvent *D*) gave, on concentration, 3-deoxy-1,2:5,6-di-*O*-isopropylidene-*α*-D-*erythro*-hex-3-enofuranose (**32**; 0.03 g, 6.4%), mp 49–50° (from hexane), R_F 0.7 (solvent *D*); lit.[37] mp 48–50°. NMR data: ^{1}H, δ 6.08 (d, 1 H, H-1), 5.30 (ddd, 1 H, H-2), 5.25 (dd, 1 H, H-3), 4.59 (ddt, 1 H, H-5), 4.15 (dd, 1 H, H-6a), 3.97 (dd, 1 H, H-6b), 1.47, 1.46, 1.45, and 1.39 (4 s, each 3 H, 2 CMe_2); $J_{1,2}$ 5.2, $J_{2,3}$ 2.3, $J_{2,5}$ 1.3, $J_{3,5}$ 1.3, $J_{5,6a}$ 6.8, $J_{5,6b}$ 5.8, $J_{6a,6b}$ 8.6 Hz; ^{13}C, δ 160.1 (s, C-4), 112.4, 110.4 (2 s, CMe_2), 106.6 (d, C-3), 99.0 (d, C-1), 83.4, 71.3 (2 d, C-2,5), 67.0 (t, C-6), 28.3, 28.0, 26.3, and 25.6 (4 q, 4 CH_3).

*3-Chloro-3-deoxy-1,2 : 5,6-di-*O*-isopropylidene-α-*D*-allo-furanose* (**6**).—*N*-Chlorosuccinimide (0.64 g) was added in small portions to a solution of **2** (0.5 g), Ph_3P (1.01 g), and imidazole (0.33 g) in chlorobenzene (40 mL) boiling under reflux. The mixture was processed as described for **5**, to give, after column chromatography (solvent *E*) and concentration of the fraction having R_F 0.65 (solvent *D*), **6** (0.29 g, 53.7%), mp 51–52° (from hexane), $[\alpha]_D^{20}$ +40° (*c* 0.5); lit.[13] mp 52°, $[\alpha]_D^{22}$ +41°. The ^{1}H- and ^{13}C-NMR data were in agreement with those published[12,13].

The fraction having R_F 0.75 (solvent *D*) gave, on concentration, 6-chloro-6-deoxy-1,2 : 3,5-di-*O*-isopropylidene-α-*D*-glucofuranose (**9**; 0.05 g, 9.3%), isolated as a syrup, $[\alpha]_D^{20}$ +34°; lit.[13] $[\alpha]_D^{22}$ +36°. The ^{1}H- and ^{13}C-NMR data were in agreement with those published[13,21b].

The fraction having R_F 0.7 (solvent *D*) gave, on concentration, 3-deoxy-1,2 : 5,6-di-*O*-isopropylidene-α-*D*-*erythro*-hex-3-enofuranose (**32**; 0.04 g, 8.5%).

*6-Bromo-6-deoxy-1,2 : 3,5-di-*O*-isopropylidene-α-*D*-glucofuranose* (**8**).—(*a*) Triphenylphosphine (1.0 g) was added to a solution of **2** (0.5 g) and *N*-bromosuccinimide (0.68 g) in acetonitrile (15 mL). The mixture was boiled under reflux for 3 h, then concentrated, and a solution of the residue in $CHCl_3$ was processed as described for **4** to give, after column chromatography (solvent *E*), **8** (0.45 g, 77.6%).

(*b*) The mixture of **2** (0.25 g), Ph_3P (0.49 g), and *N*-bromosuccinimide (0.34 g) in toluene (25 mL) was boiled under reflux for 2 h, then cooled, washed with aq 5% $NaHCO_3$, dried, and concentrated to give, after column chromatography (solvent *E*), **8** (0.20 g, 64.5%).

(*c*) Triphenylphosphine (0.49 g) was added to a cooled solution of *N*-bromosuccinimide (0.34 g) in *N*,*N*-dimethylformamide (7 mL). After 10 min, **2** (0.25 g) was added, and, after 3 h, the mixture was heated to 100° for 2 h, then cooled, diluted with aq 5% $NaHCO_3$ (2 mL), and concentrated. A solution of the residue in Et_2O was processed as described in (*a*), to give **8** (0.25 g, 81.0%).

(*d*) Triphenylphosphine (0.24 g) was added in small portions to a cooled solution of *N*-bromosuccinimide (0.16 g) in *N*,*N*-dimethylformamide (3 mL). After 10 min, a solution of **25** (0.2 g) in *N*,*N*-dimethylformamide (2 mL) was added. The cooling bath was removed and, after 15 min, when the conversion **25** → **27** was complete [R_F 0.3 → 0.0 (solvent *D*)], the mixture was heated at 70° for 2 h and processed as in (*c*) to give **8** (0.2 g, 80.6%).

(*e*) To a cooled solution of **25** (0.2 g) and *N*-bromosuccinimide (0.16 g) in *N*,*N*-dimethylformamide (5 mL) was added Ph_3P (0.24 g) in small portions. After 30 min, when the phosphonium salt **28** [R_F 0.3 → 0.0 (solvent *D*)] was formed, the mixture was heated to 50° for 50 min and then processed as in (*c*), to give **8** (0.21 g, 84.7%).

N,N-Dimethylsuccinimidomethaniminium bromide (**16**).—Triphenylphosphine (1.05 g) was added in small portions to a cooled solution of *N*-bromosuccinimide (0.71 g) in *N*,*N*-dimethylformamide (3 mL). The reaction was followed by NMR

spectroscopy. After 5 min, only **16** could be detected besides Ph_3PO. For NMR data, see formula **19**.

*1,2 : 3,4-Di-*O*-isopropylidene-6-*O*-triphenylphosphonio-α-*D*-galactopyranose bromide* (**21**).—To a cooled solution of **20** (0.52 g) and *N*-bromosuccinimide (0.71 g) in *N*,*N*-dimethylformamide (5 mL) was added triphenylphosphine (1.05 g) in small portions. The reaction was followed by NMR spectroscopy and was complete after 10 min. For NMR data, see Tables I and II.

*6-Bromo-6-deoxy-1,2 : 3,4-di-*O*-isopropylidene-α-*D*-galactopyranose* (**22**).—To a cooled solution of *N*-bromosuccinimide (0.53 g) in *N*,*N*-dimethylformamide (7 mL) was added Ph_3P in small portions. After 10 min, the temperature was raised to room temperature and a solution of **20** (0.52 g) in *N*,*N*-dimethylformamide (3 mL) was added. After 2.5 h when the formation of **23** [R_F 0.0 (solvent *D*)] was complete {the salt partially decomposed in TLC to give the *O*-formyl derivative **24** [R_F 0.65 (solvent *D*)]}, the mixture was heated for 2.2 h at 80°, when TLC indicated the conversion into **22** to be complete. The mixture was cooled, aq 5% $NaHCO_3$ (2 mL) was added, and the solution was concentrated. A solution of the semicrystalline residue in Et_2O was washed with aq 5% $NaHCO_3$, dried, and concentrated. Column chromatography (solvent *E*) of the residue gave **22** (0.5 g, 78%), mp 55–56° (from hexane), $[\alpha]_D^{20}$ −54°, R_F 0.75 (solvent *D*); lit.[23] mp 56°. NMR data: ^1H, δ 5.54 (d, 1 H, H-1), 4.64 (dd, 1 H, H-3), 4.38 (dd, 1 H, H-4), 4.33 (dd, 1 H, H-2), 3.98 (td, 1 H, H-5), 3.52 (dd, 1 H, H-6a), 3.42 (dd, 1 H, H-6b), 1.55, 1.45, 1.36, and 1.34 (4 s, each 3 H, 2 CMe_2); $J_{1,2}$ 5.0, $J_{2,3}$ 2.5, $J_{3,4}$ 7.9, $J_{4,5}$ 1.9, $J_{5,6a}$ 6.9, $J_{5,6b}$ 6.9, $^2J_{6a,6b}$ 10.1 Hz; ^{13}C, δ 109.6, 108.9 (CMe_2), 96.6 (C-1), 71.0, 70.9, 70.5 (C-2,3,4), 68.4 (C-5), 29.7 (C-6), 26.0, 25.0, 24.9, and 24.4 (CH_3). For the NMR data in *N*,*N*-dimethylformamide, see Tables I and II.

*6-*O*-(*N*,*N*-Dimethyliminiomethyl)-1,2 : 3,4-di-*O*-isopropylidene-α-*D*-galactopyranose bromide* (**23**).—To a cooled solution of *N*-bromosuccinimide (0.71 g) in *N*,*N*-dimethylformamide (5 mL) was added Ph_3P in small portions. After 5 min, a solution of **20** (0.52 g) in *N*,*N*-dimethylformamide (1 mL) was added, and the reaction was followed by NMR spectroscopy. After 20 min, the reaction was complete. For the NMR data, see Tables I and II.

*6-*O*-Formyl-1,2 : 3,4-di-*O*-isopropylidene-α-*D*-galactopyranose* (**24**).—To a cooled solution of *N*-bromosuccinimide (0.712 g) in *N*,*N*-dimethylformamide (10 mL) was added Ph_3P in small portions. After 10 min, a solution of **20** (0.52 g) in *N*,*N*-dimethylformamide (5 mL) was added, and the temperature was raised to room temperature. After 50 min, when **20** [R_F 0.3 (solvent *D*)] was converted into **23** [R_F 0.0 (*D*)] {this partially decomposed in TLC to **24** [R_F 0.65 (*D*)]}, aq 5% $NaHCO_3$ (2 mL) was added, and the solution was concentrated. A solution of the semicrystalline residue in Et_2O was washed with aq 5% $NaHCO_3$, dried, and concentrated. Column chromatography (solvent *E*) of the residue gave **24** (0.47 g, 81.6%), mp 59–60°, $[\alpha]_D^{20}$ −48°, R_F 0.65 (solvent *D*). NMR data: ^1H, δ 8.10 (s, 1 H, CHO), 5.54 (d, 1 H, H-1), 4.63 (dd, 1 H, H-3), 4.4–4.0 (m, 5 H, H-2,4,5,6a,6b),

1.52, 1.46, 1.34, and 1.33 (4 s, each 3 H, 2 CMe_2); $J_{1,2}$ 5.0, $J_{2,3}$ 2.5, $J_{3,4}$ 7.9 Hz. For the NMR data in *N,N*-dimethylformamide, see Tables I and II.

Anal. Calcd for $C_{13}H_{20}O_7$: C, 54.16; H, 6.99. Found: C, 54.22; H, 7.08.

1,2:3,5-Di-O-isopropylidene-α-D-glucofuranose (**25**).—$Bu_4NF \cdot 3H_2O$ (1.01 g) was added to a solution of **31** (1.05 g) in tetrahydrofuran (15 mL). After 50 min, Et_3N (1–2 drops) was added, and the solution was concentrated. Column chromatography (solvent *D*) of the residue gave **25** (0.71 g, 97.3%), isolated as a syrup, $[\alpha]_D^{20}$ +39°, R_F 0.3 (solvent *D*); lit.[27] $[\alpha]_D^{20}$ +40.7°. NMR data: ^1H, δ 6.00 (d, 1 H, H-1), 4.59 (d, 1 H, H-2), 4.38 (dd, 1 H, H-4), 4.19 (d, 1 H, H-3), 3.9–3.6 (m, 3 H, H-5,6a,6b), 1.97 (m, 1 H, OH), 1.49, 1.37, 1.36, and 1.33 (4 s, each 3 H, 2 CMe_2); $J_{1,2}$ 3.7, $J_{3,4}$ 3.8, $J_{4,5}$ 6.8 Hz.

6-O-tert-Butyldimethylsilyl-1,2-O-isopropylidene-α-D-glucofuranose (**30**).—$^tBuMe_2SiCl$ (0.71 g) was added to a solution of **29** (1 g) in pyridine (15 mL). After 2 h, the mixture was processed in the usual way to give, after column chromatography (solvent *E*), **30** (1.35 g, 89.4%), isolated as a syrup, which crystallised on storage and was filtered with hexane; mp 72–73°, $[\alpha]_D^{20}$ −8.0°, R_F 0.6 (solvent *D*); lit.[38] mp 62–63°. NMR data: ^1H, δ 5.96 (d, 1 H, H-1), 4.54 (d, 1 H, H-2), 4.36 (t, 1 H, H-3), 4.1–3.95 (m, 2 H, H-4,5), 3.89 (dd, 1 H, H-6a), 3.74 (dd, 1 H, H-6b), 3.30 (d, 1 H, HO-3), 2.88 (d, 1 H, HO-4), 1.48, 1.32 (2 s, each 3 H, CMe_2), 0.91 (s, 9 H, ^tBu), and 0.10 (s, 6 H, $SiMe_2$); $J_{1,2}$ 3.7, $J_{3,4}$ 2.5, $J_{5,6a}$ 3.6, $J_{5,6b}$ 5.0, $J_{6a,6b}$ 10.4, $J_{3,OH}$ 3.0, $J_{4,OH}$ 4.5 Hz.

6-O-tert-Butyldimethylsilyl-1,2:3,5-di-O-isopropylidene-α-D-glucofuranose (**31**).—To a solution of **30** (1.2 g) in acetone (25 mL) were added 2-methoxypropene (0.68 mL) and *p*TsOH (0.03 g). After 40 min, aq 5% $NaHCO_3$ (2 mL) was added, and the mixture was concentrated. Column chromatography (solvent *F*) of the residue gave **31** (1.14 g, 85.0%), isolated as a syrup, $[\alpha]_D^{20}$ +28°, R_F 0.55 (solvent *F*). NMR data: ^1H, δ 5.99 (d, 1 H, H-1), 4.56 (d, 1 H, H-2), 4.31 (dd, 1 H, H-4), 4.17 (d, 1 H, H-3), 3.82 (dd, 1 H, H-6a), 3.72 (dd, 1 H, H-6b), 3.60 (td, 1 H, H-5), 1.48, 1.35, 1.34, 1.33 (4 s, each 3 H, 2 CMe_2), 0.89 (s, 9 H, ^tBu), and 0.06 (s, 6 H, $SiMe_2$); $J_{1,2}$ 3.7, $J_{3,4}$ 3.7, $J_{4,5}$ 6.9, $J_{5,6a}$ 3.2, $J_{5,6b}$ 6.3, $J_{6a,6b}$ 11.3 Hz.

Anal. Calcd for $C_{18}H_{34}O_6Si$: C, 57.72; H, 9.15. Found: C, 57.68; H, 9.21.

General procedure for the preparation of O-formyl compounds. —To an ice-cooled and stirred solution of *N*-bromosuccinimide in *N,N*-dimethylformamide (*N,N*-dimethylacetamide for **40**) was added Ph_3P (for the ratio of the reagents, see Table III; the final concentration of the solution was 0.2 mmol of sugar/mL of solvent). After 15 min, the substrate or its solution in *N,N*-dimethylformamide was added and the cooling bath was removed. When the starting material was completely converted into the iminium type of intermediate (**17**), aq 5% $NaHCO_3$ was added, and, after 5–10 min, the mixture was concentrated under diminished pressure. A solution of the semicrystalline residue in EtOAc was washed with aq 5% $NaHCO_3$, dried, and concentrated. When the product was soluble in Et_2O, the crystalline Ph_3PO was removed, the filtrate was concentrated, and the residue was subjected to column chromatography. When the product was insoluble in Et_2O, the

TABLE III

Data for the *O*-formylated compounds

Compound	General conditions [a]	Reagent (mol. equiv.)		Yield (%)	Solvent [c]	Ref.
		Ph_3P	NBS [b]			
3	2 h, 25°	2.0	2.0	76.4	*E*	13, 41
24	50 min, 25°	2.0	2.0	81.6	*E*	21
34	1.5 h, 25°	1.2	1.2	74.3	*D*	39
36	3 h, 25°	1.1	1.1	71.2	*D*	
37	70 min, 25°	1.2	1.2	78.1	*D*	
39	3 h, 25°; 1.5 h, 80°	1.5	1.5	70.2	*D*	
40	1 h, 25°; 4 h, 50°	2.0	2.0	21.2	*D*	40

[a] See Experimental. [b] *N*-Bromosuccinimide. [c] Solvent used in column chromatography.

semicrystalline residue was dissolved in benzene and subjected to column chromatography. The yields of the *O*-formyl derivatives and the reaction conditions are given in Table III. The IR spectra contained carbonyl bonds at 1730 cm^{-1} (formyl) and that for **40** at 1750 cm^{-1} (acetyl).

6-O-Formyl-1,2-O-isopropylidene-α-D-glucofuranose (**34**).—Prepared from **29**, **34** had mp 74–76°, $[\alpha]_D^{20}$ −7.8°, R_F 0.6 (solvent *A*); lit.[39] mp 98–100°, $[\alpha]_D^{22}$ −3.5°. NMR data: ^1H, δ 8.14 (s, 1 H, CHO), 5.97 (d, 1 H, H-1), 4.55 (d, 1 H, H-2), 4.54 (d, 1 H, H-3), 4.45–4.2 (m, 3 H, H-5,6a,6b), 4.12 (dd, 1 H, H-4), 1.50 and 1.33 (2 s, each 3 H, CMe_2); $J_{1,2}$ 3.6, $J_{3,4}$ 2.8, $J_{4,5}$ 6.5 Hz.

Methyl 2,3-anhydro-6-O-formyl-α-D-mannofuranoside (**36**).—Prepared from **33**, **36** had mp 68–70°, $[\alpha]_D^{20}$ +84°, R_F 0.3 (solvent *D*). NMR data: ^1H, δ 8.15 (t, 1 H, CHO), 4.95 (s, 1 H, H-1), 4.49 (ddd, 1 H, H-6a), 4.26 (ddd, 1 H, H-6b), 4.04 (m, 1 H, H-5), 3.99 (d, 1 H, H-4), 3.90 (dd, 1 H, H-3), 3.69 (d, 1 H, H-2), 3.41 (s, 3 H, OMe), and 2.73 (b, 1 H, OH); $J_{2,3}$ 2.9, $J_{4,5}$ 7.2, $J_{3,5}$ 0.6, $J_{5,6a}$ 2.8, $J_{5,6b}$ 5.7, $J_{6a,CHO}$ 0.7, $J_{6b,CHO}$ 0.7 Hz.

Anal. Calcd for $C_8H_{12}O_6$: C, 47.06; H, 5.93. Found: C, 47.14; H, 6.02.

6-Deoxy-5-O-formyl-1,2-O-isopropylidene-β-L-idofuranose (**37**).—Prepared from **35**, **37** had mp 90–91°, $[\alpha]_D^{20}$ −49°, R_F 0.4 (solvent *D*). NMR data: ^1H, δ 8.09 (s, 1 H, CHO), 5.96 (d, 1 H, H-1), 5.32 (m, 1 H, H-5), 4.52 (d, 1 H, H-2), 4.2–4.05 (m, 2 H, H-3,4), 1.51, 1.32 (2 s, each 3 H, CMe_2), and 1.35 (d, 3 H, H-6,6,6); $J_{1,2}$ 3.7, $J_{5,Me}$ 6.4 Hz.

Anal. Calcd for $C_{10}H_{16}O_6$: C, 51.72; H, 6.95. Found: C, 51.79; H, 6.89.

1-O-Formyl-2,3 : 4,5-di-O-isopropylidene-β-D-fructopyranose (**39**).—Prepared from **38**, **39** had $[\alpha]_D^{20}$ −36°, R_F 0.7 (solvent *D*). NMR data: ^1H, δ 8.11 (t, 1 H, CHO), 4.61 (dd, 1 H, H-4), 4.51 (dd, 1 H, H-1a), 4.31 (d, 1 H, H-3), 4.25 (ddd, 1 H, H-5), 4.12 (dd, 1 H, H-1b), 3.91 (dd, 1 H, H-6b), 3.78 (d, 1 H, H-6b), 1.55, 1.49, 1.40, and 1.35 (4 s, each 3 H, 2 CMe_2); $J_{1a,1b}$ 11.7, $J_{1a,CHO}$ 0.9, $J_{1b,CHO}$ 0.6, $J_{3,4}$ 2.6, $J_{4,5}$ 7.9, $J_{5,6a}$ 1.9, $J_{5,6b}$ 0.8, $J_{6a,6b}$ 13.0 Hz.

Anal. Calcd for $C_{13}H_{20}O_7$: C, 54.15; H, 7.00. Found: C, 54.22; H, 7.13.

3-O-Acetyl-1,2:5,6-di-O-isoproylidene-α-D-glucofuranose (**40**).—Prepared from **2**, **40** had mp 60–61°, $[\alpha]_D^{20}$ −34° (*c* 0.5), R_F 0.6 (solvent *D*); lit.[40] mp 62°, $[\alpha]_D^{24}$ −38.5°.

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