Reactions of nitro sugars. VI. Nucleophilic additions and elimination–additions[1]

HANS H. BAER, THOMAS NEILSON, AND WERNER RANK
Department of Chemistry, University of Ottawa, Ottawa, Canada

Received December 20, 1966

2-Substituted methyl 3-deoxy-3-nitro-β-D-glucopyranosides were obtained in good yields by nucleophilic additions to methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-β-D-*erythro*-hexopyranos-2-enide (I) or by elimination–addition reactions with methyl 3-deoxy-3-nitro-β-D-glucopyranoside (II) or its 2-*O*-acetate III. Substituents introduced in the 2-position were the methoxy, ethoxy, benzoxy, benzylthio, diethylamino, piperidino, and *N*-(carboethoxymethyl)-amino groups.

Canadian Journal of Chemistry. Volume **45**, 991 (1967)

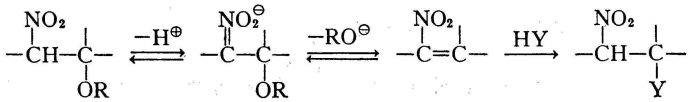
There are several reactions, all closely related and based upon the activating effect of the nitro group, that permit the introduction or exchange of substituents in the β-position in aliphatic nitro compounds. The key role in these reactions is played by α-nitroolefins, which may be either employed as such or generated *in situ* from suitable precursors. It is well known that α-nitroolefins undergo nucleophilic additions to give β-substituted nitroalkanes (reaction A). β-Acetoxynitroalkanes easily undergo base-catalyzed elimination of acetic acid, and an ensuing nucleophile addition to the intermediate olefins results in the same β-substituted nitroalkanes (reactions B + A). Furthermore, hydroxyl ions are known to catalyze a reversible interconversion between β-hydroxynitroalkanes and α-nitroolefins (reaction C) and, although the equilibrium lies on the side of the former, competing nucleophiles, under certain conditions, may cause reaction A to occur. Finally, acetal or ketal linkages involving β-nitro alcohols may be cleaved by base, and the resulting nitroolefin intermediates will react further depending on the conditions (reactions D + A).

Although there exists considerable literature, particularly on reactions A, B, and C in the realm of general aliphatic chemistry (1), there have been relatively few applications in carbohydrate chemistry. In this laboratory, reactions A and B were recently used for the synthesis of aminonitro (and thence diamino) sugars (2); reactions A, B, and C were shown to be involved in certain acetylations and postulated to play a role in epimerizations of nitro glycosides (3, 4); and reactions D and A were investigated in connection with the alkali lability of nitro sugar ketals and glycosides (5).[2] In the present paper we report on some reactions of type A, B, and C that have led to several 2-substituted methyl 3-deoxy-3-nitro-β-D-glucopyranosides.

It had been observed accidentally that recrystallization of a sample of methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-β-D-*erythro*-hexopyranos-2-enide (I) from hot ethanol gave a less-pure product, and indeed, when refluxing was continued for 2 h, I was largely converted into a new product. Elemental analysis and the infrared spectrum conformed with a methyl 4,6-*O*-benzylidene-3-deoxy-2-*O*-ethyl-3-

[1]For part V in this series, see ref. 6.

[2]Pertinent work by others is cited in refs. 2–5.



Reaction A: Y = nucleophile
Reaction B: R = $COCH_3$
Reaction C: R = H

Reaction D: R = C(R′R″)OR‴, where R′ = H or CH_3, R″ = C_6H_5 or CH_3, and R‴ = alkyl

nitro-β-D-hexopyranoside (3),[3] for which the *gluco* configuration (V) is proposed on the evidence discussed in a subsequent section. We have now obtained the 2-*O*-methyl analogue IV in the same way in an 81% yield, and the 2-*O*-benzyl analogue VI was isolated in a 47% yield when I was refluxed for 2 days in toluene that contained benzyl alcohol. It is noteworthy that these reactions can occur without added catalyst. Possibly they are promoted by traces of base present in the reagents and (or) by an inductive effect of the glycosidic center to which the nitroolefin grouping is attached.[4] The extreme facility of the addition becomes particularly evident, however, when one does provide a catalyst on purpose. Thus, the methyl ether IV was isolated in a 98% yield when a methanolic solution of I and a small amount of sodium methoxide were allowed to stand at room temperature for 5 min. The ethyl ether V was obtained in a yield of 88% under analogous conditions, but extension of the reaction time to 3 h reduced the yield to 78%. It had been observed previously (4) that the benzylidene grouping in the 2-hydroxy compound II is labile in an alkaline medium. A similar sensitivity could be anticipated in the 2-alkoxy derivatives IV and V. Actually, liberation of benzaldehyde was noticed. Although this was negligible in the case of IV, as indicated by the near quantitative yield of that compound, it certainly was a contributing factor in the diminution in the yield of V.

The nitroolefin I, if it is to be used as such in the above additions, must be prepared by a Schmidt–Rutz reaction (i.e. a dehydroacetylation with dry sodium bicarbonate in an inert solvent (1)) from the 2-*O*-acetyl glucoside III. To obtain the 2-*O*-alkyl ethers, however, the preparation of I may be circumvented. When III was heated for 1 h with sodium acetate in methanolic or ethanolic solution, IV and V were smoothly produced in yields exceeding 90%. This appears to be an excellent preparative method. Feuer and Miller (8), in studying Michael additions between simple nitroalkanes and α-nitroolefins, have shown that the latter may be formed *in situ* by the action of sodium acetate on β-nitroalkyl acetates, and that in the presence of an alcohol a nitroalkyl ether may be generated.[5] The authors (8) also proposed a mechanism for this reaction, in accordance with which the olefin I presumably is an intermediate in the conversion of III into IV. This was borne out by the smooth formation, under identical reaction conditions, of IV from methyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-deoxy-3-nitro-β-D-mannopyranoside, the 2-epimer of III. The epimer loses a molecule of acetic acid to give the same intermediate I, which then adds methanol to produce the stereochemically more favored *gluco* ether IV. An obvious analogy exists here to the *manno* to *gluco* epimerization that occurred (3) in the sodium acetate catalyzed acetylation of the 2-epimer of II.

Next, a study was undertaken to see if a direct replacement, by various functional groups, of the hydroxyl group in the nitro alcohol II is feasible. Previous experiences had shown no evidence of any spontaneous exchange of hydroxyl for methoxyl in methyl 3-deoxy-3-*aci*-nitro-glycoside sodium salts in a slightly alkaline methanolic medium at low temperature.[6] More drastic conditions seemed to be necessary to convert II into 2-substituted derivatives, but at the same time it had to be taken into account that, in hydroxylic solvents, the expected products would be prone to lose the benzylidene group by alkaline elimination (4, 5). Conversion into the 2-*O*-alkyl ethers IV and V proved successful (71–75% yields) when II and the alcohols were refluxed for 24 h in toluene solution in the

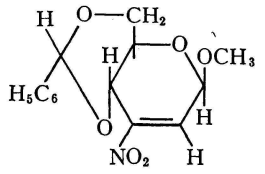
[3]Another instance of the formation of such a compound under similar circumstances was recently encountered (6).

[4]3,3,3-Trichloro-1-nitropropene is known to add alcohols without catalyst (7).

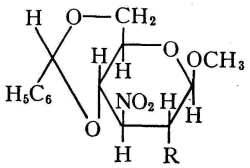
[5]1-Methoxy-2-nitrobutane was obtained in a 34% yield when 2-nitrobutyl acetate and sodium acetate were warmed in methanol for 16 h at 40°.

[6]That is, under the conditions prevailing during the synthesis of such glycosides by nitromethane cyclization of sugar dialdehydes. However, whether an exchange does in fact occur to a limited extent has not been investigated.

presence of basic[7] aluminium oxide. Using the same technique, we also prepared in good yields the 2-deoxy-2-benzylthio derivative VII, the 2-deoxy-2-diethylamino derivative VIII, the 2-deoxy-2-piperidino derivative IX, and the 2-deoxy-2-carboethoxymethylamino derivative X. Shorter reaction times were required with the addends of greater nucleophilicity.



I



II	R = OH
III	R = $OCOCH_3$
IV	R = OCH_3
V	R = OC_2H_5
VI	R = $OCH_2C_6H_5$
VII	R = $SCH_2C_6H_5$
VIII	R = $N(C_2H_5)_2$
IX	R = NC_5H_{10}
X	R = $NHCH_2CO_2C_2H_5$

[7]The reaction failed with neutral aluminium oxide.

Assignment of Configuration

Nuclear magnetic resonance spectra (60 Mc.p.s.) were obtained from deuteriochloroform solutions of compounds IV–X. The integrated spectra exhibited signals for the various substituents as expected, the chemical shifts and intensities being in accord with the gross structures (Table I).

Although most of the signals for the ring hydrogens and the hydrogens at C-6 of the methyl ether IV were crowded together in the 6 τ region and therefore were difficult to assign, the signal occurring at lowest field was a clear triplet of integrated intensity one. It was centered at 5.26 τ and split by 10.5 c.p.s. That this triplet was caused by H-3 (at the carbon bearing the nitro group) was revealed by the spectrum of compound IV deuterated at C-3 (IV-3-*d*), in which the triplet was largely removed.[8] The spacing of 10.5 c.p.s. required H-3 to be axial and coupled vicinally with two axial protons at C-4 and C-2, thus establishing the *gluco* configuration. In agreement with this assignment, a sharp doublet of intensity one, expected to be given at low field by the anomeric proton, was centered at 5.60 τ and had a spacing of 7.5 c.p.s. This signal was unchanged in compound IV-3-*d*.

[8]IV-3-*d* was obtained by the addition of methanol-d_1 to the olefin I. The sample contained a small quantity of IV, and therefore gave a weak signal for the residual H-3.

TABLE I

Chemical shifts (τ values) and relative intensities (number of protons in parentheses) in deuteriochloroform (the signals are sharp singlets unless otherwise indicated)

	Phenyl	*Ph*—CH—*O*$_2$	*O*—CH_3	*C*—CH_3	CH_2*
IV	2.55 (5)	4.46 (1)	6.40 (3) 6.48 (3)		
IV-3-*d*	2.55 (5)	4.47 (1)	6.42 (3) 6.49 (3)		
V	2.54 (5)	4.45 (1)	6.42 (3)	8.89 (3)†	
VI	2.54 (5) 2.62 (5)	4.47 (1)	6.40 (3)		
VII	2.62 (5) 2.68 (5)	4.53 (1)	6.44 (3)		
VIII	2.51 (5)	4.40 (1)	6.43 (3)	8.99 (6)†	7.25 (4)¶
IX	2.62 (5)	4.50 (1)	6.49 (3)		8.6 (6)‡ 6.9–7.8 (4)§
X	2.59 (5)	4.46 (1)	6.43 (3)	8.73 (3)†	7.5 (2)‖

*Other than C-6; the signals that were shifted below 6.5 τ are not listed.
†Triplet with a spacing of 7 c.p.s.
‡β and γ protons of piperidyl (medium broad).
§α protons of piperidyl (broad).
‖N—CH_2—CO (broad).
¶Quartet with a spacing of 7 c.p.s.

Although these data sufficed to prove the *gluco* configuration of IV, an attempt was made to obtain assignments for the remaining protons by taking the spectra in a different solvent, acetone. Despite some changes in the chemical shifts, there was little advantage in this. Again, the triplet for H-3 ($J_{3,4} = J_{2,3} = 10.5$ c.p.s.) occurred at lowest field (5.05 τ), followed by the doublet for H-1 ($J_{1,2} = 7.5$ c.p.s.) at 5.35 τ. In the spectrum of compound IV-3-*d*, the former resonance was removed and the latter remained the same. No definite assignments were possible for the other ring protons, partly because the fringe of their region was obscured by the strong methoxy resonances.

The spectrum of the thiobenzyl compound VII could be analyzed more easily, since the signal for H-2 appeared at 6.9 τ, well upfield from the other signals. It was a quartet with $J_{1,2} = 8.5$ c.p.s. and $J_{2,3} = 11.7$ c.p.s. A doublet with a spacing of 8.5 c.p.s. for the anomeric proton H-1 was found at 5.6 τ, and the signal at lowest field, a quartet centered at 5.45 τ, was assigned to H-3 ($J_{2,3} = 11.7$ c.p.s. and $J_{3,4} = 9.7$ c.p.s.). Again, the couplings required axial dispositions of H-1, H-2, H-3, and H-4, and hence proved the *gluco* configuration. Low-field triplets or quartets attributable to H-3, with large splittings of 10–12 c.p.s. that indicated axial–axial proton interactions, were also present in the spectra of V, VI, VIII, IX, and X, as were doublets attributable to H-1 with splittings of 7–9 c.p.s.

The stereochemical course of the reactions described in this paper is in line with some concurrent observations made in this laboratory. Thus, in reactions of aqueous ammonia with either I (in ethyl acetate) or III (in tetrahydrofuran) the *gluco* configuration was strongly favored in the product obtained (2), and in the addition of isopropyl lactate (in toluene) to I the *gluco* adduct was isolated exclusively and in a high yield (9).

EXPERIMENTAL

Compounds I, II, and III were prepared as described previously (10). Melting points were taken in capillaries in an electrically heated aluminium block apparatus equipped with a calibrated thermometer. All evaporations were carried out *in vacuo* at 35–40° (bath temperature). Infrared spectra were obtained by the Nujol mull technique on a Perkin-Elmer Infracord instrument, and the most characteristic absorption bands are listed at the end of this section.

Addition of Alcohols to Methyl 4,6-Benzylidene-2,3-dideoxy-3-nitro-β-D-erythro-hexopyranos-2-enide (I)

(a) By Heating I with Alcohols

Methyl 4,6-O-benzylidene-3-deoxy-2-O-methyl-3-nitro-β-D-glucopyranoside (IV).—Nitroolefin I (500 mg) was gently boiled under reflux in 50 ml of methanol for 2 h. Concentration of the solution to a small volume caused crystallization of the methyl ether IV as beautiful needles (450 mg, 81%), m.p. 183–184°. Recrystallization from methanol raised the melting point to 186°, $[\alpha]_D^{23}$ −58° (*c*, 1 in dimethylformamide).

Anal. Calcd. for $C_{15}H_{19}NO_7$ (325.3): C, 55.38; H, 5.89; N, 4.31. Found: C, 55.62; H, 6.02; N, 4.35.

Methyl 4,6-O-benzylidene-3-deoxy-3-deuterio-2-O-methyl-3-nitro-β-D-glucopyranoside (IV-3-d) was obtained by refluxing I (200 mg) for 2 h in an azeotropic mixture (10 ml) of methanol-d_1 and toluene. Removal of the solvent gave a colorless residue which, on crystallization from methanol, gave 150 mg of the deuterated compound, m.p. 184–185°.

Methyl 4,6-O-benzylidene-3-deoxy-2-O-ethyl-3-nitro-β-D-glucopyranoside (V).—The preparation and analysis of V have been reported (3), although no complete configuration had been assigned. For a redetermination of the physical data, a sample was carefully recrystallized from ethanol–water, and gave m.p. 126–127° and $[\alpha]_D^{23}$ −71.8° (*c*, 0.92 in ethanol). These values are in agreement with those of V obtained by different methods (see below), and supersede those reported earlier (m.p. 122–123°, $[\alpha]_D^{23}$ −88°).

Methyl 4,6-O-benzylidene-2-O-benzyl-3-deoxy-3-nitro-β-D-glucopyranoside (VI).—Nitroolefin I (500 mg) and benzyl alcohol (1 ml) were refluxed in toluene (25 ml) for 2 days. The reaction mixture was evaporated, petroleum ether (b.p. 30–60°) (25 ml) and water (100 ml) were added, and the two-phase system was left overnight in a crystallization dish. A crude solid product separated and was recrystallized from ethanol to give needles (325 mg, 47.5%), m.p. 133–134°, $[\alpha]_D^{23}$ −21° (*c*, 1 in dimethylformamide).

Anal. Calcd. for $C_{21}H_{23}NO_7$ (401.4): C, 62.83; H, 5.78; N, 3.49. Found: C, 62.79; H, 5.92; N, 3.71.

(b) By Catalysis with Sodium Alkoxide

Nitroolefin I (100 mg) was dissolved by gentle warming in 10 ml of *methanol*. After the solution was cooled to 23°, a small amount of methanol that contained approximately 3 mg of sodium was added. IV crystallized spontaneously. After 5 min the crystals were filtered off with suction and washed with cold methanol, yield 45 mg, m.p. 186–187°. The filtrate was immediately deionized with a small amount of Dowex 50W-X12 (H^+); after dilution with

more methanol, gentle warming, and removal of the resin, the filtrate was evaporated to give another 64 mg of a white solid, m.p. 170–172° (crude) and 186–187° (upon recrystallization from methanol–water). The optical rotation of the first fraction was −58.1° (*c*, 1.1 in dimethylformamide), and that of the second fraction before recrystallization was −56.2° (*c*, 1.07 in dimethylformamide). The infrared spectra were identical with that of IV prepared by method *a*. The combined yield was 98%.

An experiment similar to that just described was carried out with I (100 mg), *ethanol*, and sodium ethoxide. No spontaneous crystallization occurred because of the greater solubility of the ethyl ether V. After 7 min the solution was deionized and evaporated to give a crystalline but somewhat sticky residue that smelled slightly of benzaldehyde. Recrystallization from ethanol–water gave 101.5 mg (88%) of fine needles of V, m.p. 125–126°, $[\alpha]_D^{23}$ −72.4° (*c*, 1.06 in ethanol). The infrared spectrum was identical with that of V prepared by method *a*. When the experiment was repeated with a reaction time of 3 h, the yield was 78%, m.p. 127°, $[\alpha]_D^{23}$ −72.2° (*c*, 0.9 in ethanol).

Reaction of Methyl 2-O-Acetyl-4,6-O-benzylidene-3-deoxy-3-nitro-β-D-glucopyranoside (III) with Sodium Acetate and Alcohols

A solution of *O*-acetate III (50 mg) and anhydrous sodium acetate (50 mg) in *methanol* (5 ml) was refluxed for 1 h and then concentrated to a small volume, whereby crystallization began. An equal volume of water was added, and the crystals were collected and washed with water to give 42 mg (91%) of IV, m.p. 186–187°. That this product was identical with IV prepared as described in the preceding section was ascertained by comparison of the infrared spectra and by an undepressed mixture melting point. A mixture melting point with III was strongly depressed (143–155°).

An experiment similar to that just described was carried out with III (100 mg) and anhydrous sodium acetate (100 mg) in *ethanol* (10 ml); 92 mg (96%) of V with m.p. 126–127° was obtained. That this product was identical with V prepared as described in the preceding section was confirmed by comparison of the infrared spectra and by an undepressed mixture melting point.

Equal amounts of methyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-deoxy-3-nitro-β-D-mannopyranoside (3) and anhydrous sodium acetate were refluxed for 30 min in approximately 100 parts of *methanol*. The yellow solution was treated with activated charcoal, and then water was added to incipient crystallization. Fine needles melting at 185–186° were collected in a good yield. The product was shown to be IV by its infrared spectrum and an undepressed mixture melting point.

Reaction of Nucleophiles with Methyl 4,6-O-Benzylidene-3-deoxy-3-nitro-β-D-glucopyranoside (II)

All reactions were performed by heating the reactants under reflux in toluene in the amounts and for the periods of time specified. The toluene had been dried over anhydrous calcium sulfate, and the reflux condenser was equipped with a drying tube. The aluminium oxide used was "$Al_2O_3 + H_2O$, reagent grade, suitable for chromatographic adsorption, pH (slurry 10:100) 10.0–10.5".[9] The progress of the reactions was followed by thin-layer chromatography on silica gel G plates (2.5 × 7 cm) that were irrigated with methyl ethyl ketone–*n*-heptane (6:4 v/v) and sprayed with ceric sulfate–sulfuric acid reagent. Starting material (II) was run on each plate for comparison. The chromatograms revealed complete or almost complete absence of II in the reaction mixtures after the periods of time indicated. Filtration and evaporation *in vacuo* then gave products that were recrystallized as specified.

Methyl 4,6-O-Benzylidene-3-deoxy-2-O-methyl-3-nitro-β-D-glucopyranoside (IV)

The reactants were II (200 mg), aluminium oxide (600 mg), and methanol (0.5 ml) in toluene (20 ml). After 7 h another 0.5 ml of methanol was added. The total reaction time was 24 h. The yield, upon recrystallization from methanol (ca. 15 ml), was 149 mg (71%) of IV, m.p. 186°, $[\alpha]_D^{23}$ −57.4° (*c*, 1.13 in dimethylformamide). That this product was identical with IV obtained previously was confirmed by infrared spectroscopy and by an undepressed mixture melting point.

Methyl 4,6-O-Benzylidene-3-deoxy-2-O-ethyl-3-nitro-β-D-glucopyranoside (V)

The reactants were II (100 mg), aluminium oxide (300 mg), and ethanol (0.5 ml) in toluene (10 ml). The reaction time was 24 h and the yield of crude V melting at 119–120° was 82 mg (75%). Recrystallization from ethanol gave fine needles (75 mg, 69%), m.p. 125–126.5°, $[\alpha]_D^{23}$ −71.6° (*c*, 0.74 in ethanol). The infrared spectrum and an undepressed mixture melting point confirmed that the product was identical with V described previously.

Methyl 4,6-O-Benzylidene-2-benzylthio-2,3-dideoxy-3-nitro-β-D-glucopyranoside (VII)

The reactants were II (311 mg), aluminium oxide (1 g), and thiobenzyl alcohol (0.4 ml) in toluene (30 ml). The reaction time was 3 h and the yield of VII (needles after crystallization from ethanol–water (1:1), m.p. 149–151°) was 310 mg (76.5%). Recrystallization from the same solvent raised the melting point to 154–155°.

Anal. Calcd. for $C_{21}H_{23}NO_6S$ (417.5): C, 60.44; H, 5.54; S, 7.68. Found: C, 60.62; H, 5.72; S, 7.66.

Methyl 4,6-O-Benzylidene-2,3-dideoxy-2-diethylamino-3-nitro-β-D-glucopyranoside (VIII)

The reactants were II (100 mg), aluminium oxide (300 mg), and diethylamine (0.5 ml) in toluene (10 ml). The reaction time was 3 h. A yellow syrup was obtained which was crystallized from ethanol–water to give 85 mg (72%) of VIII, m.p. 118–119°, $[\alpha]_D^{23}$ −9° (*c*, 1.5 in ethanol).

[9]Manufactured by Shawinigan Chemical Co. Distributed by the McArthur Chemical Co. Ltd., Montreal.

Anal. Calcd. for $C_{18}H_{26}N_2O_6$ (366.4): C, 59.00; H, 7.16; N, 7.65. Found: C, 59.23; H, 7.26; N, 7.73.

The same product was obtained readily in a good yield from *O*-acetate III in tetrahydrofuran and diethylamine by an adaptation of the nitroamine synthesis described elsewhere (2).

Methyl 4,6-O-Benzylidene-2,3-dideoxy-3-nitro-2-piperidino-β-D-glucopyranoside (IX)

The reactants were II (200 mg), aluminium oxide (400 mg), and piperidine (0.5 ml) in toluene (20 ml). The reaction time was 3 h and the crude product, IX, which was crystallized from ethanol–water, weighed 187 mg. Upon recrystallization from the same solvent, the product (163 mg, 67.5%) melted at 95–100°. The melting point was raised to 118° by one further recrystallization, and then remained constant.

Anal. Calcd. for $C_{19}H_{26}N_2O_6$ (378.4): C, 60.30; H, 6.93; N, 7.40. Found: C, 60.51; H, 6.85; N, 7.48.

Methyl 4,6-O-Benzylidene-2-carboethoxymethylamino-2,3-dideoxy-3-nitro-β-D-glucopyranoside (X)

The reactants were II (200 mg), aluminium oxide (400 mg), and ethyl glycine (about 500 mg) in toluene (20 ml). In this experiment, the product and II had equal R_f values on the thin-layer chromatographic plate. A reaction time of 2 h was allowed. Crystalline X (193 mg, 76%) was obtained from ethanol, m.p. 164–166°.

Anal. Calcd. for $C_{18}H_{24}N_2O_8$ (396.4): C, 54.52; H, 6.12; N, 7.06. Found: C, 54.77; H, 6.18; N, 6.90.

Infrared Absorption Bands (cm^{-1})

IV: 1 550 and 1 370 (NO_2); 1 090, 1 070, 1 005, 985, and 960 (C—O—C); 755 and 703 (aromatic).

V: 1 555 and 1 380 (NO_2); 1 093, 1 080, 995, and 980 (C—O—C); 770–755 and 700 (aromatic).

VI: 1 545 and 1 375 (NO_2); 1 090, 1 070, 1 040, 975, and 965 (C—O—C); 750 and 693 (aromatic).

VII: 1 555 and 1 380 (NO_2); 1 095, 1 073, 993, 977, and 940 (C—O—C); 765, 715, and 700 (aromatic and C—S—C).

VIII: 1 570 and 1 380 (NO_2); 1 090, 1 007, 985, and 923 (C—O—C); 752 and 700 (aromatic).

IX: 1 560 and 1 380 (NO_2); 1 095, 1 060, 1 000, and 920 (C—O—C); 755 and 702 (aromatic).

X: 3 330 (NH); 1 725 (ester CO); 1 550 and 1 365 (NO_2); 1 215 (ester C—O—C); 1 090, 1 075, 1 030, and 1 000 – 980 (C—O—C); 755 and 700 (aromatic).

ACKNOWLEDGMENTS

The authors are grateful for the financial support from Merck and Company, Rahway, New Jersey, which enabled them to initiate this study. The work was completed with support from the National Research Council of Canada. The kind interest in the nuclear magnetic resonance spectra shown by Prof. R. R. Fraser is appreciated.

REFERENCES

1. V. V. PEREKALIN. Unsaturated nitro compounds. *Translated by* L. Mandel. Oldbourne Press, London. 1964.
2. H. H. BAER and T. NEILSON. J. Org. Chem. In press.
3. H. H. BAER, F. KIENZLE, and T. NEILSON. Can. J. Chem. **43**, 1829 (1965).
4. H. H. BAER and F. KIENZLE. Ann. **695**, 192 (1966).
5. H. H. BAER and W. RANK. Can. J. Chem. **43**, 3330 (1965).
6. H. H. BAER and F. KIENZLE. Can. J. Chem. This issue.
7. I. THOMPSON, S. LOULOUDES, R. FULMER, F. EVANS, and H. BURKETT. J. Am. Chem. Soc. **75**, 5006 (1953).
8. H. FEUER and R. MILLER. J. Org. Chem. **26**, 1348 (1961).
9. H. H. BAER and F. KIENZLE. 153rd Meeting, American Chemical Society, Miami Beach, Florida, 1967. Abstr. C50.
10. H. H. BAER and T. NEILSON. Can. J. Chem. **43**, 840 (1965).

This article has been cited by:

1. Aditya Kumar Sanki, Tanmaya Pathak. 2003. Synthesis of anomerically pure vinyl sulfone-modified pent-2-enofuranosides and hex-2-enopyranosides: a group of highly reactive Michael acceptors for accessing carbohydrate based synthons. *Tetrahedron* **59**:36, 7203-7214. [CrossRef]
2. Bernd Becker. 2000. Review Article: Anionic Conjugate Addition Reactions for the Preparation of Substituted Monosaccharides and Disaccharides. *Journal of Carbohydrate Chemistry* **19**:3, 253-284. [CrossRef]
3. Tohru Sakakibara, Ichiro Matuo, Aya Takaide, Takanori Nakamura, Akinori Seta. 1992. Experimental and Theoretical (AM1) Studies on Photoaddition Reactions of 3-Nitro-2-enopyranoside Derivatives. *Chemistry Letters* :1, 177-180. [CrossRef]
4. Tohru Sakakibara, Noriaki Ohkita, Toshio Nakagawa. 1992. Reactivities of 2-C- and 3-C-Nitro-.ALPHA.- and .BETA.-D-erythro-Hex-2-enopyranoside Derivatives towards Methanol and AM1 Studies upon Their Stereoselectivities. *Bulletin of the Chemical Society of Japan* **65**:2, 446-451. [CrossRef]
5. Peter Jütten, Hans-Dieter Scharf. 1991. An improved synthesis of evernitrose. *Carbohydrate Research* **212**, 93-108. [CrossRef]
6. Hans Paulsen, Monika Brieden, Volker Sinnwell. 1985. Verzweigte und kettenverlängerte Zucker, XXVIII. Synthese von 6-Amino-6-desoxyhepturonsäuren. *Liebigs Annalen der Chemie* **1985**:1, 113-128. [CrossRef]
7. Tetsuyoshi Takamoto, Tohru Sakakibara, Motoji Matsumoto, Rokuro Sudoh. 1977. Synthesis of phenyl 4-O-acetyl-2-O-benzyl-3-deoxy-3-nitro-β-d-glucopyranoside derivatives and amination at C-4. *Carbohydrate Research* **53**:1, 129-133. [CrossRef]
8. Johannes H. Jordaan, Jacobus J. Nieuwenhuis, Gerhardus J. Lourens. 1976. Olefinic intermediates in the synthesis of branched-chain pyranosides by the nitromethane route. *Carbohydrate Research* **51**:2, 195-206. [CrossRef]
9. Hans Paulsen, Wilfried Greve. 1973. Phosphorhaltige Kohlenhydrate, VI. Synthese von Aminozuckerphosphonaten durch Addition von Dialkylphosphiten an Nitroolefin-Zucker. *Chemische Berichte* **106**:7, 2114-2123. [CrossRef]
10. F.J.-M. Rajabalee. 1973. Synthèse de dérivés aminés du méthyl-3-désoxy-3-nitro-α- et β-d-glucopyranoside. *Carbohydrate Research* **26**:1, 219-224. [CrossRef]
11. Gerhardus J. Lourens. 1971. Preparation of branched-chain nitro and amino sugars by application of the nitromethane method to ketoses1. *Carbohydrate Research* **17**:1, 35-43. [CrossRef]
12. K.D. Carlson, C.R. Smith, I.A. Wolff. 1970. Unsaturated nitro sugars. Preparation of 4-O-acetyl-1,2-dideoxy-3,5-O-ethylidene-1-nitro-d-erythro-pent-1-enitol. *Carbohydrate Research* **13**:3, 391-402. [CrossRef]
13. Kenneth D. Carlson, Cecil R. Smith, Ivan A. Wolff. 1970. N.M.R. spectra and benzene-induced solvent shifts. Acetylated carbohydrates substituted with 1,3-O-ethylidene or nitro groups. *Carbohydrate Research* **13**:3, 403-415. [CrossRef]
14. W.A. Szarek, D.G. Lance, R.L. Beach. 1970. Addition of nitryl iodide to unsaturated carbohydrate derivatives. *Carbohydrate Research* **13**:1, 75-81. [CrossRef]
15. C. O. Carenberg, C.-G. Hed#n. 1970. Experiments with lysis of living cells ofEremothecium ashbyii and ofMethanomonas by microbial enzymes. *Biotechnology and Bioengineering* **12**:2, 167-178. [CrossRef]
16. Hans H. Baer, Farouk Rajabalee. 1970. Synthesis of derivatives of 2,3-diamino-2,3-dideoxy-α-d-glucose and 2,3,4-triamino-2,3,4-trideoxy-α-d-glucose. *Carbohydrate Research* **12**:2, 241-251. [CrossRef]
17. Roy L. Whistler, R.E. Pyler. 1970. Synthesis of 6-amino-6-deoxy-5-thio-d-glucopyranose. *Carbohydrate Research* **12**:2, 201-210. [CrossRef]
18. Toshio Nakagawa, Tohru Sakakibara, Satoru Kumazawa. 1970. Polyamino sugars IV. A synthesis of a new type of nucleosides: methyl 4,6--benzylidene-2,3-dideoxy-3-nitro-2-(7′-theophyllinyl)-β-D-glucopyranoside and its 2-(2′,6′-dichloro-9′-purinyl) homolog. *Tetrahedron Letters* **11**:19, 1645-1648. [CrossRef]
19. F. W. Lichtenthaler, P. Voss, N. Majer. 1969. Ein neuer Zugang zu Inosatriaminen und Triaminozuckern. *Angewandte Chemie* **81**:6, 221-222. [CrossRef]
20. B.E. Davison, R.D. Guthrie. 1969. Methyl 4,6-O-benzylidene-3-cyano 2,3-dideoxy-α-D-erythro-hex-2-enopyranoside and its addition reactions. *Carbohydrate Research* **9**:2, 254-255. [CrossRef]
21. T.D. InchNuclear Magnetic Resonance Spectroscopy in the Study of Carbohydrates and Related Compounds **2**, 35-82. [CrossRef]
22. Gerhardus J. Lourens. 1969. A new route to branched-chain sugars by application of the nitromethane method to ketoses. *Tetrahedron Letters* **10**:42, 3733-3736. [CrossRef]
23. Hans H. BaerThe Nitro Sugars **24**, 67-138. [CrossRef]
24. R.J. FerrierUnsaturated Sugars **24**, 199-266. [CrossRef]