nitroalkenes with $NaBH_4$, the maintenance of acidic conditions is necessary to prevent dimerization.[4]

By using the sodium borohydride procedure, the nitro nitrates listed in Table I were converted to the corresponding saturated nitro compound. The yields given are based on a single run only, and so are probably not optimal.

Table I

Reaction of Vicinal Nitro Nitrates (NN) with Sodium Borohydride

Nitro nitrate	Product	Reaction time, hr	Mol of $NaBH_4$/mol of NN	Yield, %
1-Nitro-2-octyl nitrate	1-Nitrooctane (1)	19	3.3	94
4-Methyl-1-nitro-2-pentyl nitrate	1-Nitro-4-methylpentane (2)	24	3.2	72
1-Nitro-2,4,4-trimethyl-2-pentyl nitrate	1-Nitro-2,4,4-trimethylpentane (3)	60	3.6	83
3-Nitro-2,4,4-trimethyl-2-pentyl nitrate	No reaction	41	4.3	0
1-Nitro-2-tetradecyl nitrate	1-Nitrotetradecane (4)	25	3.9	58

The nitroalkanes **1**, **2**, and **4** have ir and nmr spectra like those previously recorded[4] (ir absorption at 6.45 and 7.25 μ; nmr triplets at δ 4.35–4.37). 1-Nitro-2,4,4-trimethylpentane (**3**) gives an ABX pattern at δ 4.21 for the protons adjacent to the nitro group and a complex multiplet at δ 2.38 for the tertiary proton.

Only starting material was obtained from the reaction of 3-nitro-2,4,4-trimethyl-2-pentyl nitrate with sodium borohydride. The steric hindrance of the nitro olefin derived from this internal nitro nitrate may be too great to permit its formation.

Experimental Section

The nitro nitrates were prepared as previously described.[6] Ir spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer and nmr spectra were obtained on a Varian Associates Model V-4311 spectrometer operating at 60 Mc.

1-Nitro-2,4,4-trimethylpentane (3). General Procedure.—Sodium borohydride (1.25 g) was slowly added to a solution of 2.00 g of 1-nitro-2,4,4-trimethyl-2-pentyl nitrate in 50 ml of 95% ethanol. The mixture was stirred briefly at room temperature and allowed to stand for 2.5 days. It was diluted with H_2O (100 ml), acidified with 1.2 N HCl, and extracted with ether. The extract was washed (NaCl solution), dried ($MgSO_4$), and evaporated. 1-Nitro-2,4,4-trimethylpentane (**3**) (1.20 g, 83%) remained as a pale yellow liquid. The ir spectrum is nearly identical with that of an analytical sample prepared by chromatography on silica gel using mixtures of methylene chloride and hexane as eluents, $n^{20}D$ 1.4317. *Anal.* Calcd for $C_8H_{17}NO_2$: C, 60.3; H, 10.8; N, 8.8. Found: C, 60.2; H, 10.7; N, 8.8.

Nitroalkanes 1, 2, and 4, all colorless liquids, were prepared similarly using the conditions stated in Table I.

Registry No.—**1,** 629-37-8; **2,** 14424-33-0; **3,** 30344-80-0; **4,** 4609-87-4; sodium borohydride, 16940-66-2.

Acknowledgments.—We wish to thank Mr. Lewis P. Larson and Mr. George A. Taylor for recording the nmr spectra and Mr. Paul J. McMahon for technical assistance.

Photolysis of Penta-*O*-acetyl-*aldehydo*-D-glucose[1]

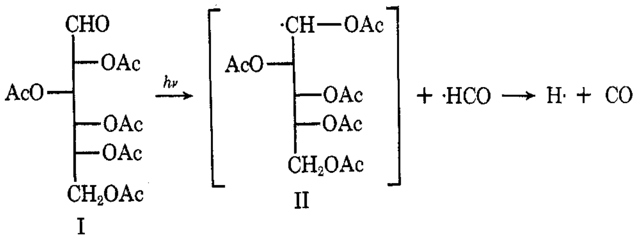
Roy L. Whistler* and Khong-Seng Ong

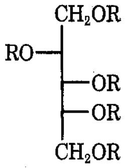
Department of Biochemistry, Purdue University, Lafayette, Indiana 47907

Received February 12, 1971

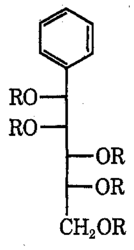
Although photodecarbonylation of aliphatic aldehydes occurs readily in the vapor phase,[2,3] elimination of carbon monoxide is almost entirely suppressed in solution at 25°. At temperatures above 100°, however, decarbonylation has been observed with quantum efficiency.[4]

It is interesting to observe, therefore, that when a benzene solution of *aldehydo*-D-glucose pentaacetate (I) is irradiated with ultraviolet light at 10–15°, it produces three major crystalline photoproducts, all of which are derived by way of radical II, realized through α-bond cleavage. Compounds III, IV, and V are formed in 16, 2.5, and 1% yield, respectively. At 60° the starting material is consumed in 6 hr as compared to 70 hr at 10–15° and the yields of III, IV, and V increase to 17.5, 6, and 2%, respectively. The small increase in yields might be due to the loss of radical II through secondary reactions which may also be temperature dependent. The formation of III is, as with aliphatic aldehydes, most prominent and is formed by α-bond fission producing carbon monoxide and a five-carbon radical that combines with a hydrogen atom to produce D-arabinitol pentaacetate, identified by comparison of mixture melting point and ir and nmr spectra with an authentic sample.[5] The nmr spectrum of photoproduct IV gives, in addition to the charac-

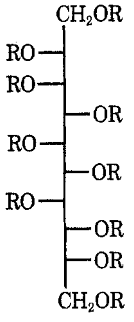




III, R = OAc
VI, R = H



IV, R = OAc
VII, R = H



V, R = OAc
VIII, R = H

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[1] This work was presented in part before the 161st Meeting of the American Chemical Society, Los Angeles, Calif., March 1971; Journal Paper No. 4338 of the Purdue Agricultural Experiment Station, Lafayette, Ind. 47907.

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teristic chemical shifts of a glycitol acetate in the τ 4.0–8.5 region, a peak at τ 2.68 attributable to a phenyl group. The proof of configuration of IV, as 1-*C*-phenylpenta-*O*-acetyl-D-*manno*-pentitol, comes from its deacetylation to the known[6] 1-*C*-phenyl-D-*manno*-pentitol (VII). The configuration at C-2 of the pentitol pentaacetate IV is thus ascertained. Though photochemical amidation[7] and acylation[8] of benzene have been observed, intermolecular alkylation as in the formation of IV is uncommon.

Dimerization of radical II to V generates new asymmetric centers at C-5 and C-6, giving rise to the possible formation of any, if not all, of the three isomeric decaacetates: D-*gluco*-D-*manno*-, D-*manno*-D-*manno*-, and D-*gluco*-L-*gulo*-decitol. The dimer crystallized as a single compound as evidenced by tlc and sharp melting point. To obtain configurational information, decitol VIII, derived from deacetylation of V, was subjected to periodate oxidation. Schwarz[9] has earlier demonstrated that oxidation of hexitols with a limited quantity (0.1 mol equiv) of periodate induces preferential cleavage between vicinal hydroxyls in the *threo* configuration. When the decitol VIII is oxidized with 0.1 mol equiv of periodate at 20°, the only sugars detected on paper chromatography are D-glucose and D-arabinose. The absence of D-mannose in the oxidized products allows tentative assignment to the decitol of the D-*gluco*-L-*gulo* configuration as shown in VIII.

Experimental Section

Irradiations were made with a 450-W 679A-36 mercury lamp without filter under oxygen-free nitrogen. The progress of reactions and purity of products were checked by thin layer chromatography (tlc) on silica gel G[10] coated glass plates (5 × 13 cm) irrigated with benzene–ether (1:2 v/v). Melting points were determined on a Fisher–Johns apparatus and were corrected. Infrared spectra were recorded in Nujol with a Perkin-Elmer Model 337 spectrometer, and nmr spectra were determined in deuteriochloroform solution with TMS as the internal standard using a Varian A-60 spectrometer. Mass spectroscopy was obtained with a Hitachi RMU-6A spectrometer at 200° (75 eV). Optical rotations were measured at 25° in a Perkin-Elmer automatic polarimeter Model 141.

Photolysis of Penta-*O*-acetyl-*aldehydo*-D-glucose.[11]—A solution of the pentaacetate I (15 g) in 1.5 l. of benzene was irradiated for 70 hr (at 10–15°), after which the solution was concentrated to dryness to give a syrup. Investigation of the syrup on tlc showed, besides starting material (R_f 0.18), three main products, corresponding to compounds V, III, and IV with R_f 0.30, 0.59, and 0.70, respectively. There was a considerable amount of tailing. The syrup was applied to a silica gel[12] column (600 g) and eluted with benzene–ether (3:1 v/v). Progress was checked by tlc and the fraction containing starting material I was crystallized from benzene–hexane: yield 2 g.

1-*C*-Phenylpenta-*O*-acetyl-D-*manno*-pentitol (IV) and 1-*C*-Phenyl-D-*manno*-pentitol (VII).—The fraction containing IV was crystallized from ethyl acetate–hexane to give pure IV: mp 92–93°; $[\alpha]^{25}\text{D}$ +28.6° (*c* 1.0, chloroform); yield 0.67 g (4.5%); τ ($CDCl_3$) 2.68 (phenyl), 5.80 (H-5), 4.3 (H-1, H-2, H-3, and H-4), 7.90, 7.96, 8.22 (OAc).

Anal. Calcd for $C_{21}H_{26}O_{10}$: C, 57.53; H, 5.97. Found: C, 57.71; H, 5.92.

Compound IV (0.4 g) was deacetylated in absolute methanol (10 ml) with a catalytic amount (0.1 ml) of 0.1 *N* sodium methoxide at 25°. On deionization with Amberlite IR-120 ion-exchange resin, compound VII thus obtained was recrystallized from ethanol–acetone: mp 172–173°; $[\alpha]^{25}\text{D}$ −46.8° (*c* 1.0, pyridine) [lit.[6] mp 172.5–173°; $[\alpha]\text{D}$ −44.8° (*c* 0.76, pyridine)].

Penta-*O*-acetyl-D-arabinitol (III).—The fraction containing III was crystallized from benzene–hexane: mp 75°; $[\alpha]^{25}\text{D}$ +37° (*c* 2.0, chloroform); yield 1.92 g (16%). Nmr and ir spectra and mixture melting point were identical with those of an authentic sample prepared from D-arabinitol. Deacetylation of III in absolute methanol gave D-arabinitol, mp 103–104° (lit.[13] mp 103°).

D-*gluco*-L-*gulo*-Decitol Decaacetate (V). A. From Column Chromatography.—The fraction containing the dimer V was crystallized from methanol: mp 156–157°; $[\alpha]^{25}\text{D}$ +55.9° (*c* 2.0, chloroform); yield 0.12 g (1%); ν_{max} 1750 cm^{-1} (OAc); mass spectrum *m/e* 662 (M − HOAc) (calcd *m/e* 722); osmometric mol wt 708.

B. From Fractional Crystallization.—In subsequent reactions where the photolyses were done for longer periods when all the starting material was consumed, the resulting syrup, when taken up in benzene, gave V as crystalline residue, prior to column chromatography.

Anal. Calcd for $C_{30}H_{42}O_{20}$: C, 49.86; H, 5.85. Found: C, 49.58; H, 5.78.

D-*gluco*-L-*gulo*-Decitol (VIII).—Decaacetate V (0.40 g) was deacetylated at 25° in neat methanol (10 ml) with a catalytic amount (0.1 ml) of sodium methoxide (0.1 *N*) to give decitol VIII, crystallized from aqueous ethanol: mp 178–179°; $[\alpha]^{25}\text{D}$ −5.2 (*c* 0.70, water); yield 0.152 g; ν_{max} 3500 and 3380 cm^{-1} (OH).

Anal. Calcd for $C_{10}H_{22}O_{10}$: C, 39.74; H, 7.34. Found: C, 40.02; H, 7.44.

Photolysis of Penta-*O*-acetyl-*aldehydo*-D-glucose at Higher Temperature.—Benzene (150 ml) was irradiated while the immersion well was circulated with water; after 3 hr an ambient temperature of 60° had been reached. Pentaacetate I (1.5 g) was then introduced in one addition and irradiation was continued for 6 hr, after which the starting material had been consumed as evidenced by tlc. The syrup, obtained after concentrating the benzene, was chromatographed on silica gel column (90 g). Photoproducts III, IV, and V, after crystallization from the specific solvents as described above, were obtained in the yields of 17.5, 6, and 2% respectively.

Sodium Periodate Oxidation of VIII.—A 0.1 *M* aqueous solution of the decitol (0.1 ml) was mixed with an equal volume of 0.01 *M* sodium periodate at 20°. After 0.5 hr the solution gave a negative starch–KI test for periodate.

Paper Chromatography of the Oxidized Decitol.—Descending technique and Whatman No. 1 paper were used and developed with ethyl acetate–pyridine–water (8:2:1 v/v). The sugars were detected with *p*-anisidine hydrochloride. Oxidized decitol gave a pink spot and a yellowish brown spot, showing that the components moved at the same rate as D-arabinose and D-glucose, respectively. In addition there was a faint spot with an R_f larger than pentose; no mannose could be detected.

Registry No.—I, 3891-59-6; III, 5401-55-8; IV, 30469-99-9; V, 30545-63-2; VII, 30469-85-3; VIII, 30469-86-4.

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