# Photolysis of Methyl 2,3,4-Tri-*O*-acetyl-6-azido-6-deoxy-α-D-glucopyranoside[1]

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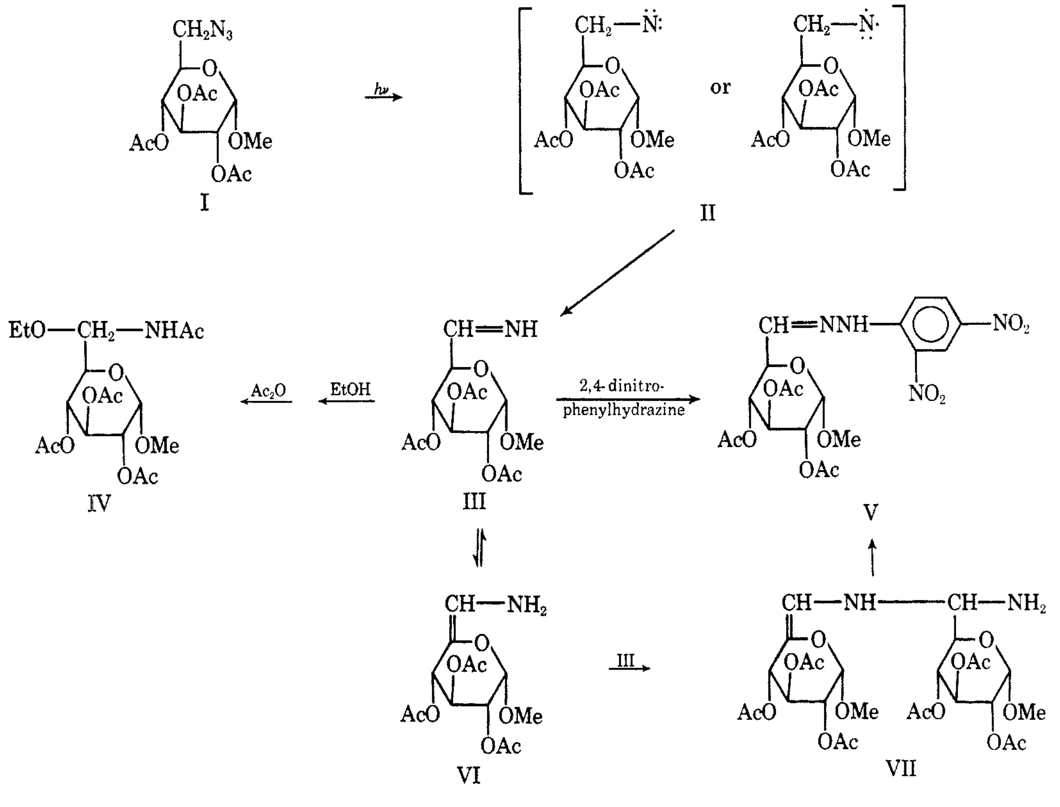
Ultraviolet irradiation of methyl 2,3,4-tri-*O*-acetyl-6-azido-6-deoxy-α-D-glucopyranoside (I) in cyclohexene gave as the main product methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-imino-α-D-glucopyranoside (III) and a small amount of its dimer. Photolysis of I in ethanol followed by acetylation of the product produced methyl 2,3,4-tri-*O*-acetyl-6-*C*-acetamido-6-*O*-ethyl-α-D-glucopyranoside (IV).

Recently, there has been awakening interest in the photochemistry of azides,[2-4] resulting in the isolation of a variety of products.[5-11] The reactive intermediate in the decomposition of the azides is the electron-deficient species, $\mathrm{R{-}\ddot{N}}$: (or $\mathrm{R{-}\dot{N}\cdot}$), commonly known as nitrenes but also termed[3] azylenes, azacarbenes, imine radicals, and imido intermediates. Like the carbenes, the nitrenes are highly unstable and pass to stable compounds by abstraction of hydrogen,[5] aryl groups,[6,7] or alkyl[6] groups from adjacent carbon atoms to give imines, by hydrogen abstraction from the solvents to produce amines,[5] by 1,5 hydrogen shift and cyclization of the diradical to yield pyrrolidines,[5] by dimerization to azo compounds,[8] or by insertion into carbon–hydrogen[4,5] or carbon–carbon double bonds.[4,10]

Although the stabilization of a nitrene may be realized by reaction with a carbon–carbon double bond, methyl 2,3,4-tri-*O*-acetyl-6-azido-6-deoxy-α-D-glucopyranoside (I) does not react with cyclohexene during photolysis with ultraviolet light. Instead, it produces the imine III and another compound which is possibly the dimer VII. The imine III is stable when kept in the solid state, but in chloroform solution it rapidly changes to a mixture consisting mainly of its dimer, as examined by tlc using ethyl acetate as the irrigant. The infrared spectrum of the imine III shows peaks at 3300 (NH), 1750 (OAc), and 1630 $\text{cm}^{-1}$ (C=N). The compound III is converted into the known 2,4-dinitrophenylhydrazone V, and the physical constants (melting point, nmr spectrum) of this derivative agree with those reported.[12] The dimerization of the imine III is explained by assuming that a second molecule of the compound III reacts with its tautomeric form VI to produce the dimer VII. Similar dimerization



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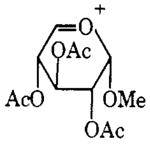
has been postulated by Hasek, *et al.*,[13] in the formation of *N*-isobutylidene-2-methylpropenylamine from *N*,*N*-diisobutylidene-2-methyl-1,1-propanediamine. The dimer, on treatment with an acidic solution of 2,4-dinitrophenylhydrazine, gives the 2,4-dinitrophenylhydrazone V.

When the compound I is irradiated with ultraviolet light in dry ethanol under nitrogen, a compound, $C_{15}H_{25}NO_9$, is isolated[14] whose infrared spectrum in Nujol shows peaks at 3360 (NH), 3250 (broad OH), 1750 (OAc), 1650, and 1530 cm$^{-1}$ (NAc). The hydroxyl peak shifts to 3600 cm$^{-1}$ when the absorption is measured in a dilute solution in chloroform, and the acetamide peak at 1650 cm$^{-1}$ is shifted to 1680 cm$^{-1}$. The mass spectrum shows a molecular-ion peak at *m/e* 363 and a mass peak at *m/e* 345 (M − 18) confirming the presence of a hydroxyl group. Peaks at *m/e* 116, 46, and 43 correspond to the fragments EtOCHNHAc, EtO, and Ac, respectively.

Thus, it appears that an acetyl group migrates to the initially formed imino groups in III and that ethanol is then added. The formation of a stable compound by addition of ethanol to a C=NAc group has been reported.[15] Acetylation of the photolysis product gives a crystalline compound which no longer shows hydroxyl absorption in the infrared. The mass spectrum still shows peaks at *m/e* 116, 46, and 43, but also shows a parent-ion peak at *m/e* 405 and a strong peak at *m/e* 289 corresponding to M − 116 (VIII). On the basis of this information, the acetylated compound is assigned the structure IV.



VIII

## Experimental Section

Irradiation was made with a 250-W Hanovia 654-A-36 mercury lamp under oxygen-free nitrogen. The completion of reactions and purity of products were determined by thin layer chromatography (tlc) on silica gel G[16] coated glass plates irrigated by ethyl acetate–hexane (1:1, v/v), ether, or ethyl acetate. The infrared (ir) spectra were determined in Nujol with a Perkin-Elmer Model 337 spectrometer, and nmr spectra were determined in $CDCl_3$ with a vapor pressure osmometer, Model 301A. Mass spectra were obtained by use of an LKB Type 900 gas chromatograph–mass spectrometer. Melting points were corrected and were determined on a Fisher-Johns apparatus. Evaporations were done under reduced pressure with a bath temperature below 25°.

**Methyl 2,3,4-Tri-*O*-acetyl-6-azido-6-deoxy-α-D-glucopyranoside (I).**—Methyl α-D-glucopyranoside was converted into its 6-tosyl derivative.[17a] The latter, after crystallization from ethyl acetate, had mp 124°. The tosyl derivative was treated then with sodium azide, acetic anhydride, and pyridine, according to literature procedure,[17b] to give the azide I, mp 103° (lit.[18] mp 103°).

**Irradiation of the Azide I in Cyclohexene.**—A solution of the azide I (6 g) in anhydrous and freshly distilled cyclohexene (1300 ml) was irradiated for 4 hr at 15–20°. The product (2.2 g) which crystallized was a mixture of methyl 2,3,6-tri-*O*-acetyl-6-deoxy-6-imino-α-D-glucopyranoside (III) and its dimer VII, as shown by tlc using ethyl acetate or ether as the irrigant. More of this mixture (1.5 g) was obtained by evaporating the solvent, dissolving the residue in ether (20 ml), and diluting with hexane (20 ml). The imine III (2 g), isolated by crystallization from ether, had mp 144–145°; $\nu_{max}$ 3300, 1750, and 1630 cm$^{-1}$; $[\alpha]^{25}\text{D}$ +185.3° (*c* 1.5, EtOAc). In chloroform, its specific rotation changes from 195 to 200° during 1 hr.

*Anal.* Calcd for $C_{13}H_{19}NO_8$: C, 49.19; H, 6.03; N, 4.41. Found: C, 49.00; H, 6.01; N, 4.27.

The dimer VII (0.5 g) was purified by chromatography on silica gel[18] using ether as the eluent. After crystallization from ether–hexane, the compound had mp 129°; $\nu_{max}$ 3300 (NH), 1750 (OAc), and 1650 cm$^{-1}$ (C=C); mass spectrum *m/e* 700 (M) (calcd *m/e* 634.6); $[\alpha]^{25}\text{D}$ +210° (*c* 1, $CHCl_3$). The dimer was hygroscopic and decomposed on storage.

*Anal.* Calcd for $C_{26}H_{38}N_2O_{16}$: C, 49.19; H, 6.03; N, 4.41. Found: C, 48.78; H, 5.83; N, 4.04.

**Methyl 2,3,4-Tri-*O*-acetyl-6-aldehydo-α-glucohexadialdo-1,5-pyranoside 6-[(2,4-Dinitrophenyl)hydrazone] (V).**[12] **A. From the Imine III.**—The imine III (170 mg) in methanol (10 ml) was reacted with 2,4-dinitrophenylhydrazine (85 mg) in a mixture of 2 *N* hydrochloric acid (15 ml) and methanol (20 ml). The reaction mixture was stirred for 5 min, diluted with water (100 ml), and cooled. The yellow precipitate of the hydrazone V (85 mg), after crystallization from methanol, had mp 168° (lit.[12] mp 168°); $[\alpha]^{25}\text{D}$ +128° (*c* 2, $CHCl_3$); $\nu_{max}$ 3200 (NH), 1730 (OAc), 1610 (C=N), and 1520 cm$^{-1}$ ($NO_2$).

**B. From the Dimer.**—Compound VII (27 mg) in methanol (5 ml) was treated with 2,4-dinitrophenylhydrazine (14 mg) in 2 *N* hydrochloric acid solution (5 ml). The solution was stirred for 5 min and the hydrazone V was isolated as described above, mp 168°, no depression when mixed with the previously obtained hydrazone.

**Irradiation of the Azide I in Ethanol.**—Compound I (4 g) in anhydrous ethanol (1300 ml) was irradiated at 26° for 3.5 hr. Most of the solvent was removed and the residue (30 ml) was cooled, whereupon 0.4 g of crystals deposited. The compound, after crystallization from ethanol, had mp 200–215° dec; $[\alpha]^{25}\text{D}$ +105.2° (*c* 1, $CHCl_3$); $\nu_{max}$ 3360, 3250, 1750, 1650, and 1530 cm$^{-1}$; nmr $\tau$ 8.80 (t, $-CH_3$ of OEt, $J$ = 7.2 Hz), 8.00, 7.96, 7.92 (9 acetyl H), 6.00–6.80 (8 H), 5.20–4.30 (4 H) and 3.67 (1 H); mass spectrum (70 eV) *m/e* 363, 345, 116, 46, and 43.

*Anal.* Calcd for $C_{15}H_{25}NO_9$: C, 49.58; H, 6.93; N, 3.85. Found: C, 49.45; H, 6.92; N, 3.80.

The photolysis product (15 mg) thus obtained was acetylated in pyridine (0.5 ml) and acetic anhydride (0.3 ml) at 25° for 16 hr. The mixture was evaporated to produce 15 mg of a crystalline residue. This was recrystallized from chloroform-hexane to give 12 mg of methyl 2,3,4-tri-*O*-acetyl-6-*C*-acetamido-6-*O*-ethyl-α-D-glucopyranoside (IV): mp 180°; $[\alpha]^{25}\text{D}$ +107.7° (*c* 0.3, $CHCl_3$); $\nu_{max}$ 3320 (NH), 1745, 1725 (OAc), 1665, and 1510 cm$^{-1}$ (NAc); mass spectrum (70 eV) *m/e* 405, 289, 116, 46, and 43.

*Anal.* Calcd for $C_{17}H_{27}NO_{10}$: C, 50.35; H, 6.71; N, 3.45. Found: C, 50.29; H, 6.72; N, 3.49.

**Registry No.**—I, 21893-05-0; III, 21893-06-1; IV, 21893-07-2; VII, 21893-08-3.

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