

THE LIGHT-INDUCED ADDITION OF 1,3-DIOXOLAN TO UNSATURATED CARBOHYDRATES

J.S. Jewell and W.A. Szarek

Department of Chemistry, Queen's University,  
Kingston, Ontario, Canada

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The increased availability in recent years of methods for the preparation of unsaturated carbohydrates (1) has stimulated interest in addition reactions to these compounds. In this laboratory (2) the application of the Wittig reaction with alkylidene phosphoranes to aldehydo and keto sugar derivatives has been achieved to prepare olefinic substrates; the keto compounds afford branched-chain unsaturated carbohydrates. Photochemical additions of thiolacetic acid (3) and of phosphines (4) to 5,6-dideoxy-1,2-O-isopropylidene- $\alpha$ -D-xylo-hex-5-enofuranose (I) have been reported. We now describe the light-induced addition in the presence of acetone of 1,3-dioxolan to compound I, and to a new branched-chain unsaturated sugar (VI) prepared by way of a Wittig reaction (2). The products of the photochemical reactions were the 2-substituted 1,3-dioxolans. The formation of the 1:1 anti-Markownikoff adducts and their acid-catalyzed hydrolysis to aldehydes constitute a versatile one-carbon, chain-extension procedure in sugar synthesis. Acetone-initiated photochemical additions of 1,3-dioxolan to olefins have been reported previously by Elad and Rosenthal (5).

A mixture of compound I (6) (0.62 g), 1,3-dioxolan (20 ml), and acetone (1 ml), to which acetone (5 ml) had been added in 1-ml portions at 2-hr intervals, was irradiated\* for 24 h. The solution was concentrated to dryness, and the residue was chromatographed on silica gel to give, in addition to some unchanged starting material and a non-carbohydrate derivative, syrupy 2-(5'-deoxy-1',2'-O-isopropylidene- $\alpha$ -D-xylo-hexofuranos-6'-yl)-1,3-dioxolan (II): yield 0.39g (45% based on starting olefin);  $[\alpha]_D^{26} -10^{\circ}$  (c 0.5, chloroform);

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\* Irradiations were performed in pyrex tubes with a Rayonet Photochemical Chamber Reactor using a complete set (sixteen) of 2537 Å lamps.

R<sub>F</sub> 0.19 (thin layer chromatography on Silica Gel G, 3:3:1 benzene-chloroform-ether); nmr,  $\tau$  4.10 (1-proton doublet,  $J_{1',2'} = 3.8$  Hz, H-1'), 5.05 (1-proton multiplet, -OCH<sub>0</sub>-), 5.48 (1-proton doublet, H-2'), 8.17-8.31 (4-proton multiplet, C-5' and C-6' methylenes). Compound II was formulated as a 2-substituted 1,3-dioxolan by comparison of its nmr data with that of authentic 2- and 4-alkyl-1,3-dioxolans (5).

Irradiation as above of a mixture of 3-deoxy-1,2:5,6-di-0-isopropylidene-3-methyl-ene- $\alpha$ -D-ribo-hexofuranose (VI) and 1,3-dioxolan in the presence of acetone gave the 1:1 adduct VII as a syrup (55%):  $[\alpha]_D^{26} +50^\circ$  (c 0.5, chloroform); nmr,  $\tau$  4.27 (1-proton doublet,  $J_{1',2'} = 3.8$  Hz, H-1'), 4.98 (1-proton triplet, -OCH<sub>0</sub>-), 5.35 (1-proton triplet,  $J_{2',3'} = 3.8$  Hz, H-2'), 7.85-8.05 (3-proton multiplet, H-3' and exocyclic methylene). The allo configuration for compound VII was assigned by nmr spectroscopy. In 1,2-0-isopropylidene- $\alpha$ -D-xylo-hexofuranose derivatives, the coupling between H-2 and H-3 is very small and results in the spectral pattern for H-2 being a doublet (7). In the nmr spectrum of VII, however, H-2' appeared as a triplet, which collapsed to a doublet with a spacing of 3.8 Hz when H-1' was irradiated. Thus, H-2' is coupled to H-3' with  $J_{2',3'} = 3.8$  Hz, and the configuration must be allo. A value of 4 Hz for  $J_{2,3}$  in 1,2:5,6-di-0-isopropylidene- $\alpha$ -D-allofuranose has been reported (8).

The branched-chain unsaturated sugar VI was obtained by the reaction of methylene-triphenylphosphorane with 1,2:5,6-di-0-isopropylidene- $\alpha$ -D-ribo-hexofuranos-3-ulose (IV). The Wittig reaction was performed in ether, and involved preparing the ylid in liquid ammonia with sodium amide as the base and then replacing ammonia by ether (2). Compound VI was obtained as an analytically pure syrup by distillation, bp 90-100° (bath)/0.2 torr;  $[\alpha]_D^{26} +75^\circ$  (c 1.0, chloroform); nmr,  $\tau$  4.22 (1-proton doublet,  $J_{1,2} = 3.8$  Hz, H-1), 4.45-4.65 (2-proton multiplet, 2 vinyl H's), 5.19 (1-proton doublet, H-2).

The 3-ketone IV was prepared by oxidation of 1,2:5,6-di-0-isopropylidene- $\alpha$ -D-glucofuranose (III) with methyl sulfoxide-acetic anhydride (9). Removal of the reagents by evaporation at low temperature (10) gave a mixture of IV and a small amount

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\* Nuclear magnetic resonance (nmr) spectra were measured at 60 MHz in chloroform-d with tetramethylsilane as the internal standard.

of a new compound, 1,2:5,6-di-O-isopropylidene-3-O-(methylthio)methyl- $\alpha$ -D-glucofuranose (V). Compound V was isolated as a syrup by preparative gas-liquid chromatography:  $[\alpha]_D^{26} -15^\circ$  ( $c$  0.3, chloroform); nmr,  $\tau$  4.18 (1-proton doublet,  $J_{1,2} = 3.8$  Hz, H-1), 5.30 (2-proton singlet, OCH<sub>2</sub>S), 5.45 (1-proton doublet, H-2), 7.85 (3-proton singlet, SMe). Treatment of V with Raney nickel in ethanol gave 1,2:5,6-di-O-isopropylidene-3-O-methyl- $\alpha$ -D-glucofuranose (11). The formation of (methylthio)methyl ethers, by treatment of 1,2:3,4-di-O-isopropylidene- $\alpha$ -D-galactopyranose (12) and various noncarbohydrate alcohols (13) with methyl sulfoxide-acetic anhydride, has been reported recently.

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