COMMUNICATIONS

Photochemistry of Glycosyl Azides

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Irradiation with u.v. light of a methanolic solution of β-D-glucopyranosyl (**1**), α-D-mannopyranosyl (**3**), or β-D-galactopyranosyl (**4**) azide affords in good yield the corresponding next-lower aldose. In the case of β-maltosyl (**6**), β-D-ribofuranosyl (**7**), or α-L-arabinopyranosyl (**8**) azide, there was observed the formation of an intermediate which, on standing in the dark, reverts back to starting material.

L'irradiation avec de la lumière ultra-violette d'une solution méthanolique d'azothydrure de β-D-glucopyrannosyle (**1**), d'α-D-mannopyrannosyle (**3**) ou de β-D-galactopyrannosyle (**4**), a conduit avec des bons rendements aux aldoses immédiatement inférieurs correspondants. Dans le cas des azothydrures de β-maltosyle (**6**), de β-D-ribofurannosyle (**7**) ou d'α-L-arabinopyrannosyle, on a observé la formation d'un intermédiaire qui redonne le produit initial lorsqu'on le laisse à la noirceur.

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The photochemistry of various types of organic azides has been extensively studied (1). Generally, photolysis of azides results in elimination of molecular nitrogen and formation of products which can be rationalized by the intermediacy of a nitrene (for reviews on nitrenes see ref. 2), although the existence of such an intermediate has not been proven in all cases. A variety of reactions is available to photochemically-generated nitrenes, namely, abstraction of hydrogen by the nitrene, rearrangement of a hydrogen or carbon function to the electron-deficient nitrogen, and insertion of the nitrene into a saturated bond or addition to multiple bonds. In the field of carbohydrate chemistry, it has been found that photolysis of primary azides in sugar systems, followed by mild hydrolysis of the resultant imino derivatives, is an excellent method for the preparation of ω-aldehydo derivatives of glycosides (3), 6-aldehydo analogs of such polysaccharides as amylose (4, 5), starch (4), and cellulose (6, 7), and 5′-aldehyde analogs of nucleosides (8); the photolysis presumably occurs by way of an intermediate nitrene ($R—CH_2N:$) which rearranges by a 1,2-hydrogen migration. Photolysis of secondary azides of sugars also leads to carbonyl derivatives, but the yields of the keto sugars are low (9). In this Communication we report some results of an investigation of the photochemistry of glycosyl azides. Two salient features of this work are the facile degradation by u.v. light of some of the azides to the corresponding next-lower aldose, and the observation, in some cases, of the formation of an intermediate which, on standing in the dark, reverts back to starting material.

The first type of behavior was exhibited by aldohexopyranosyl azides. The experiments involved irradiation[3] of a solution of the glycosyl azide[4] (1.5 g) in methanol (65 ml) for 4 h, at the end of which time t.l.c. on silica gel (1:2:3, v/v, methanol – ethyl acetate – benzene or 3:1 ethanol–benzene) indicated that all of the starting material had been consumed, and showed the presence of a slower-moving component and a nonmigrating component; the reaction mixture was concentrated, and the former component

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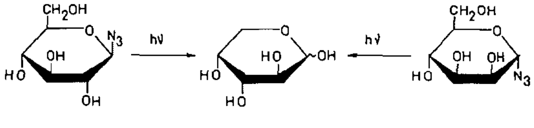
[3] Irradiations were performed with a 450-W Hanovia medium-pressure mercury-arc lamp (Cat. No. 679A-36) contained in a water-cooled, quartz immersion-well; a Vycor 7010 filter-sleeve was employed. The whole assembly was mounted in a borosilicate glass reaction-vessel.

[4] Details of the preparation of the glycosyl azides employed in the study described in this Communication, together with their physical constants, will be reported later. As a typical example, β-D-galactopyranosyl azide (**4**) exhibits weak absorption in its u.v. spectrum (methanol) at 275 nm (ε 38.4).

was isolated by column chromatography. Thus, β-D-glucopyranosyl azide (**1**) and α-D-mannopyranosyl azide (**3**) afforded D-arabinose (**2**) in 47 and 60% yields, respectively, whereas β-D-galactopyranosyl azide (**4**) gave D-lyxose (**5**) in 65% yield.



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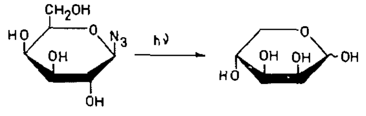

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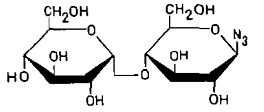
When 4-*O*-α-D-glucopyranosyl-β-D-glucopyranosyl azide (**6**, β-maltosyl azide) was irradiated under the conditions described above, t.l.c. (2:3, v/v, benzene–ethanol) again indicated after 4 h that all of the starting compound had been converted into a slower-moving material, which was revealed as an elongated spot suggestive of the presence of more than one compound, and a nonmigrating component. The i.r. spectrum of the reaction mixture (determined with a smear obtained by rapidly evaporating a small aliquot) did not show any absorption at ~2130 cm^{-1} attributable to an azido group, but showed a broad band centered at ~1670 cm^{-1}. However, after the reaction mixture had been kept for 2 h in the dark, the i.r. spectrum showed a weak absorption at 2125 cm^{-1}. After 50 h, a very strong absorption attributable to an azido group was observed in the spectrum; moreover, t.l.c. indicated the presence of a considerable amount of starting material.[5] Column chromatography afforded 0.91 g of the starting azide (**6**) and 0.40 g of slower-moving material. The i.r. spectrum of the latter showed a broad band at ~1670 cm^{-1}; acid-catalyzed hydrolysis of this material afforded glucose and arabinose, a result which suggests the presence of some 3-*O*-α-D-glucopyranosyl-D-arabinose, the disaccharide expected to be formed by photochemical degradation of β-maltosyl azide (**6**). The identity of the substance giving rise to the absorption at ~1670 cm^{-1} has not been established. It is noteworthy that, whereas during the irradiation of the aldohexopyranosyl azides **1**, **3**, and **4** there was an immediate and steady evolution of gas, in the case of β-maltosyl azide (**6**) very little gas appeared to be liberated.



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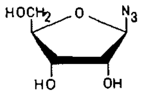

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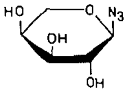

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The unusual behavior exhibited by β-maltosyl azide, namely, the formation upon irradiation of an intermediate which, on standing in the dark, reverts back to starting material, was also observed with β-D-ribofuranosyl azide (**7**) and α-L-arabinopyranosyl azide (**8**). In the latter two cases the presence of starting material could not be detected by t.l.c. after 2 h of irradiation; longer periods of irradiation resulted in severe streaking of the chromatograms.

The results described in this Communication indicate that the irradiation with u.v. light of appropriate glycosyl azides should be a convenient one-carbon, chain-shortening procedure (for other photochemical degradations of carbohydrate derivatives see ref. 10) in synthetic carbohydrate chemistry. An investigation of the second type of behavior is in progress.

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[5] The same observations were recorded on irradiating β-maltosyl azide (6) for 11 h and then keeping the reaction mixture in the dark for 48 h.

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Direct Formation of the Carbonyl Anion of Diisopropyl Formamide[1]

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The reaction of diisopropyl formamide with lithium diisopropylamide produces, by abstraction of the formyl proton, the carbonyl anion, $LiCON[CH(CH_3)_2]_2$. Reactions of this anion with benzaldehyde, benzophenone, ethyl benzoate, acetone, and propionaldehyde occur in yields ranging from 30–92%. Thus, this anion provides a useful method for the synthesis of α-hydroxy and α-keto acids, particularly in cases where cyanohydrin formation is difficult.

La réaction de la diisopropyl formamide avec la diisopropylamide de lithium a produit, par enlèvement du proton formyle, l'anion carbonyle $LiCON[CH(CH_3)_2]_2$. Les réactions de cet anion avec de la benzaldéhyde, de la benzophénone, du benzoate d'éthyle, de l'acétone et de la propionaldéhyde se font avec des rendements variant de 30–92%. Par suite grâce à cet anion on obtient une méthode utile pour la synthèse de α-hydroxy et α-cétoacides, particulièrement dans les cas où la formation de cyanohydrines est difficile. [Traduit par le journal]

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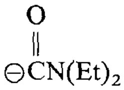
Recently much work (1) has been devoted to the formation of carbanions whose utility in synthesis derive from their being "carbonyl anion equivalents" (2). Naturally it would be much easier and more valuable if carbonyl anions could be directly formed and reacted. There is evidence in the literature that this should be possible. Both alkoxide (3*a*) and amide (3*b*) anions undergo reversible addition to carbon monoxide at high pressure. Alkyllithiums have also been shown to add to carbon monoxide (3*c*). Furthermore, Schöllkopf and Gerhart (4) have postulated the carbanion of diethylformamide  $\ominus\overset{\displaystyle O}{\overset{\|}{C}}N(Et)_2$ as the probable intermediate[2] in the conversion of the mercuriamide, $Hg[CON(Et)_2]_2$ by reaction with butyllithium and benzophenone into the hydroxyamide $(C_6H_5)_2C(OH)CON(C_2H_5)_2$. We wish to report a new method of formation of an acyl carbanion, specifically, by direct abstraction of the formyl proton of diiso-

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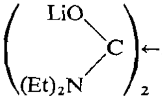
[1] Support for this work by the National Research Council of Canada is gratefully acknowledged.

[2] Alternatively, the intermediate involving coordination of mercury to the carbene form of the anion, *i.e.*,  $\left(\begin{array}{l}LiO\\ \quad\;\;\rangle C\\ (Et)_2N\end{array}\right)_2\leftarrow Hg—(n\text{-}Bu)_2$ was suggested (4).