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SYNTHETIC STUDIES OF CARBOHYDRATE DERIVATIVES WITH THE PHOTOCHEMICAL REACTION I. PHOTOCHEMICAL ADDITION OF THIOACETIC ACID, BENZYL MERCAPTAN AND 1,3-DIOXOLANE.

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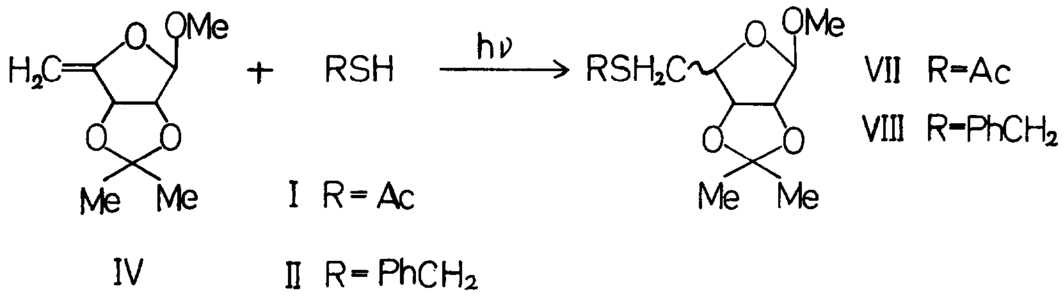
The photochemical addition reaction of mercaptans to olefines is known to proceed efficiently by irradiation with the light of under 300 mμ wave length in the presence of a photosensitizer such as acetone(1). A sole application of the procedure to the addition reaction of an analogous reagent to unsaturated sugars was reported by Horton and Turner(2), i. e., the reaction of thioacetic acid to 5,6-dideoxy-1,2-O-isopropylidene-α-D-*xylo*-hex-5-enofuranose, which carries a terminal exocyclic double bond in its structure, affords the corresponding 1 : 1 adduct in 54% yield. Whereas, the photochemical addition of 1,3-dioxolane to terminal double bond(3) was extended by Jewell and Szarek(4) also to the carbohydrate region.

In view of such situation, the present work was undertaken in our laboratory with an expectation that these reactions may serve as an unique procedure for the preparation of sulfur containing or branched-chain sugar derivatives. The authors wish to report in the present communication on the photochemical addition reaction of thioacetic acid (I), benzyl mercaptan (II) and 1,3-dioxolane (III) to unsaturated sugars, i. e., methyl 5-deoxy-2,3-O-isopropylidene-β-D-*erythro*-pent-4-enofuranoside (IV), 2,3,4,6-tetra-O-acetyl-2-hydroxy-D-glucal

(V) and 3,4,6-tri-O-acetyl-D-glucal (VI).

Addition of thioacetic acid and benzyl mercaptan

On irradiation of a solution of IV (1.05 g) in I (2 ml) and of that in II (2 ml) with ultraviolet light(5) in a quarz glass test tube under nitrogen atmosphere at room temperature for 64 hours, respectively, the corresponding 1 : 1 adducts: methyl 5-acetylthio- (VII)(6) $\{bp_{0.57}$ 75 – 80°C, $[\alpha]_D$ -43°(c 0.7, MeOH), ν_{max} 1680($Me-C\lesssim^{O}_{S-}$)$\}$ and methyl 5-benzylthio-5-deoxy-2,3-O-isopropylidene-β-D-ribo(or α-L-lyxo)-furanoside (VIII)(6) $\{bp_{0.65}$ 130 – 135°C, ν_{max} 750 and 690 (monosub. phenyl)$\}$ were obtained in 61% and 69% yield by the subsequent vacuum distillation,respectively. Entirely the same results (VII: 69% and

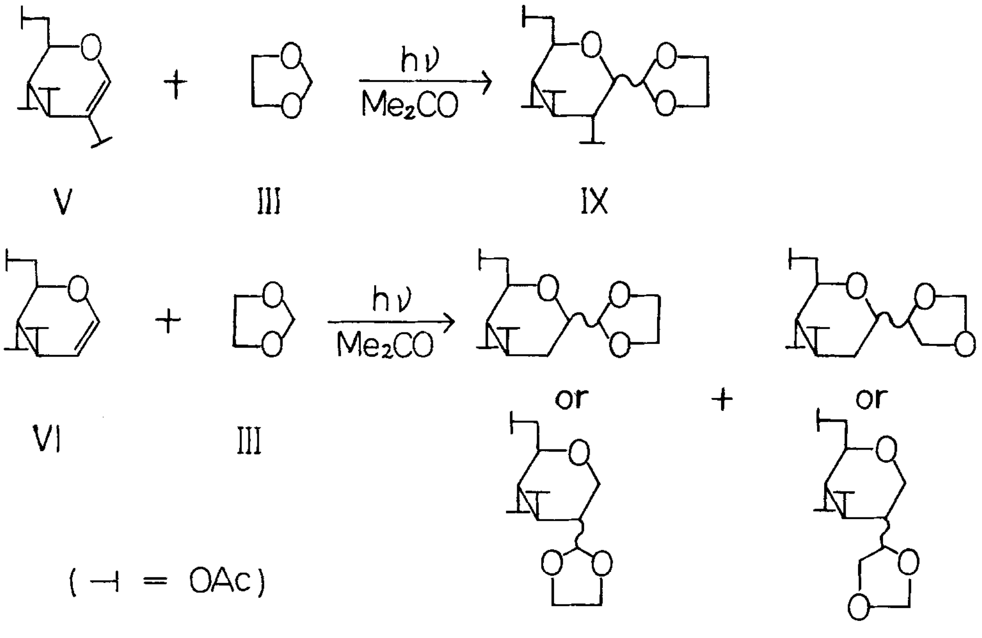


VIII: 69% yield) were obtained by the irradiation of the above solution with ultraviolet light(7) in the presence of acetone (5 ml) at room temperature for 86 hours. With respect to the configuration at C-4 position of these products, it was estimated to be of D-ribo-type rather than of L-lyxo-type on the basis of the following facts: i) The light-induced decarbonylation reaction of methyl 6-deoxy-2,3-O-isopropylidene-α-L-lyxo-hexopyranoside-4-ulose preferred the formation of D-ribo-type (92%) to that of L-lyxo-type (8%)(8). ii) The specific rotational value of VII mentioned above is virtually the same as that reported by Clayton and Hughes $\{[\alpha]_D$ -47° (0.7, MeOH)$\}$(9).

Contrary to our expectation, the same treatment of V and VI with I or II, respectively, afforded no adduct, however, these results are of much interest as comparing with the reaction induced by cumene hydroperoxide which afforded the corresponding adduct in good yield(10).

Addition of 1,3-dioxolane

A solution of V (1.0 g) in the mixture of III (10 ml) and acetone (2 ml) was irradiated with ultraviolet light(7) under nitrogen atmosphere at room temperature for 65 hours, and the volatiles were evaporated *in vacuo*. The residue was subsequently chromatographed on a silica gel column to give sirupy 2-[(2′,3′,4′,6′-tetra-O-acetyl-D-glucopyrano-1′(?)-yl]-1,3-dioxolane (IX)(6)$\{[\alpha]_D$ $+12.7°$(c 1.0, MeOH)$\}$ in 86% yield. While, the resultant mixture from the reaction of VI (1.0 g), III (10 ml) and acetone (2 ml) was evaporated *in vacuo* to a sirup, and the sirup was chromatographed similarly to give 2-[2′(or 1′)-deoxy-3′,4′,6′-tri-O-acetyl-D-glucopyrano-1′(or 2′)-yl]- (X)(6)[mass spectrum: m/e 346 (M^+), 273 (M- ·), 73 (·; the ratio of · /·Ac = 0.85)] and 4-[2′(or 1′)-deoxy-3′,4′,6′-tri-O-acetyl-D-glucopyrano-1′(or 2′)-yl]-1,3-dioxolane (XI)(6)[NMR: 5.50τ(2-proton singlet, C-2 methylene). Such signal could not be detected in the case of X; mass spectrum: m/e 345 (M-1), 317 (M-CHO), 273 (M- ·), 73 (·; the ratio of · /·Ac = 0.33)] along



V III IX

VI III X XI

(⊣ = OAc)

with the unchanged VI. The ratio of X : XI : VI in the mixture was estimated as 82 : 6 : 12 by gas liquid chromatography prior to the silica gel chromatography. An examination on the structure of X and XI, concerned with the configuration of the linkage between 1,3-dioxolane and the sugar moiety, is now in progress. In contrast with the reaction of I or II, it is noteworthy that V and VI are susceptible to addition reaction of III. Interesting to state, moreover, 4-substituted 1,3-dioxolane derivative (XI) was confirmed in the field of carbohydrate chemistry for the first time.

A further investigation on the photochemical addition reaction of some reagents to unsaturated sugar derivatives is now in progress in our laboratory in order to clarify the correlation between the properties of the reagents and the reactivity of enoses due to the position of their double bond.

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