Preliminary communication

Photochemical additions of 2,3-dimethylbut-2-ene to hexenulopyranoses

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Photochemical dimerisations of $\alpha:\beta$ unsaturated ketones and additions of olefins to the double bonds of such enones to give cyclobutane derivatives are well documented[1-3]. However, reactions with cyclic enones possessing an endocyclic oxygen atom have been little studied[4], and no report has appeared in which carbohydrate substrates have been used.

Carbohydrates appeared to be good models with which to investigate the stereochemistry of these additions and, furthermore, recent reports[5] concerning compounds in which pyranoid rings were fused to cyclopropyl rings suggested that this photochemical annelation reaction might be used to produce homologues of this class.

A 1% solution of 4,6-*O*-benzylidene-1,2-dideoxy-D-*threo*-hex-1-en-3-ulopyranose[6] (**1**) (2.5 g) in methylene chloride containing 2,3-dimethylbut-2-ene (10 g) was irradiated* ($\lambda > 290$ nm) for 1.5 h, after which time a decrease in the absorption at λ 266 nm showed that *ca.* 80% of the enone **1** had reacted. This was substantiated by (t.l.c.) examination of the gum obtained after solvent evaporation. Four products *A–D* having R_F values 0.8, 0.7, 0.5, and 0.25, respectively, were formed in high yield. Column chromatography gave homogeneous (t.l.c.) samples of *A* as a syrup (0.28 g), $[\alpha]_D$ +39°(chloroform); *B* (0.3 g), m.p. 127–128°, $[\alpha]_D$ −28°; *C* (0.8 g), m.p. 124–125°, $[\alpha]_D$ −136°; and a sample (0.2 g) composed of equal amounts of compounds *A* and *B*. Compounds *A–C* were isomeric, saturated ketones, ν_{max} 1720 cm^{-1} (enone absorptions at 1670 and 1600 cm^{-1} absent), formed by addition of the 2,3-dimethylbut-2-ene to the carbon–carbon double bond of the enone (satisfactory elemental analyses; four methyl singlets in the n.m.r. spectra, see Table I). The sample of component *D*** (1.0 g),

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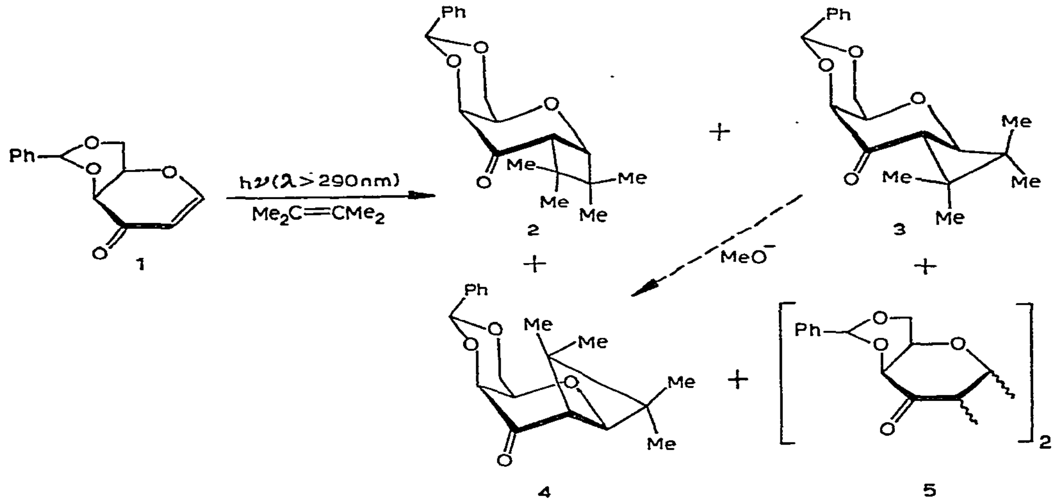
*Irradiations were carried out in the annular space of a conventional photolysis well (diameter 5 cm) with light from a 450-watt Hanovia medium-pressure mercury-arc.

**The yield of this compound was inversely proportional to the concentration of the dimethylbutene present in the photolysate, and it could be virtually eliminated when a twenty-fold excess of olefin was employed. This was accompanied by a commensurate increase in yield of addition products.



m.p. 230–235° (dec.), ν_{max} 1725 cm^{-1} (saturated ketone), molecular weight 430 (Rast), was a mixture of isomeric dimers of the type 5 which would be expected$^{1-3}$ from the photolysis of 1; it exhibited n.m.r. absorptions for benzylidene residues and broad bands for ten protons in the region δ 4.8~3.6 and two protons in the region δ 3.0~2.7.

TABLE I

CHEMICAL SHIFTS (δ) AND SPLITTINGS (Hz) FOR THE CYCLOBUTYL DERIVATIVES 2, 3, AND 4 IN C_6D_6 MEASURED AT 100 MHz[a]

Compound	*H-1*	*H-2*	*H-4*	*H-5*	*H-6*	*H-6'*	*CMe (4 singlets)*
2	4.82 (d) $J_{1,2}$ 5.5	2.89 (d) $J_{2,1}$ 5.5	3.98 (d) $J_{4,5}$ 2.5	3.53 (m) $J_{5,6'}$ 2.0	4.12(q) $J_{6,5}$ 2.0	3.45 (q) $J_{6',6}$ 13.0	1.27, 0.95, 0.87, 0.77
3	3.64 (d) $J_{1,2}$ 9.3	3.41 (d) $J_{2,1}$ 9.3	3.93 (d) $J_{4,5}$ 1.6	3.04 (m) $J_{5,6'}$ 2.0	4.19 (q) $J_{6,5}$ 1.0	3.46 (q) $J_{6',6}$ 13.0	1.19, 1.07, 0.85, 0.71
4	3.55 (d) $J_{1,2}$ 4.5	2.42 (d) $J_{2,1}$ 4.5	3.67 (d) $J_{4,5}$ 1.5	2.70 (m) $J_{5,6'}$ 2.0	4.15 (q) $J_{6,5}$ 1.0	3.48 (q) $J_{6',6}$13.0	1.28, 1.04, 0.94, 0.86

[a] PhC*H*O_2 (s) appeared in range 5.25–5.30. Aromatic signals (m) appeared in range 7.15–7.60.

Only three of the possible four stereoisomers of the olefin addition compounds were produced in the photolysis. It was shown, by the test originally employed by Corey[7], that two of these (*A* and *C*) were formed by *cis* fusion between the pyranoid ring and the cyclobutane ring, since they were unaffected by base. Compound *B*, however, was isomerized to *C* under these conditions★, indicating[7] that it possessed

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★It is noteworthy that isomerisation at C-4 did not occur in the presence of base or upon irradiation with u.v. light. This was shown by the facts that the three adducts formed from the D-*erythro* analogue were not converted into *C* by base and that their R_F values differed from those of *A* and *C* a *trans*-fused ring system. It seems most probable that the *trans* isomer, bonded diaxially at C-1 and C-2 on the $^4C_1$ pyranoid ring, was the one absent from the photolysate. Thus, compound *B* must have structure **3**, a conclusion substantiated by the large coupling between H-1 and H-2 (9.3 Hz), which is satisfactory for a compound existing in a conformation approximating to that depicted in **3**. Since **3** was transformed into *C* on basic treatment, the latter must have structure **4**. Thus, the remaining *cis*-isomer (*A*) must have structure **2**. The coupling between H-1 and H-2 in these compounds is that expected for a *cis* pair of vicinal hydrogen atoms on a pyranoid ring.

Photolysis of the D-*erythro* analogue of **1**, under similar conditions, gave (n.m.r., i.r. and t.l.c. data) a mixture of three addition products with dimethylbutene.

The mixture of *cis*- and *trans*-fused products obtained in these reactions compares with that from cyclohex-2-enone—olefin[2,6] additions (see, however, ref. 8). The product ratios for **2**:**3**:**4** were *ca.* 1:1:2, and can be most economically explained by a mechanism in which the bonds are not formed concertedly[1,2,6]. If one of the olefin carbon atoms formed a bond[9] with C-2 (carbohydrate numbering) of the excited enone **1** from above or below the plane of the pyranoid ring (giving an axial or an equatorial bond, respectively, if the pyranoid ring is in the $^4C_1$ conformation), then ring closure of the first intermediate would produce only compound **4**, whereas closure of the second one could form both **2** and **3**. There are, however, results[10] which suggest that initial bonding might occur at C-1 of the enone **1**, and this would invalidate the argument. A further possibility is that the *cis* and *trans* products arise from different excited species.

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