Ground and Excited State 1,4-Addition Reactions of some Carbohydrate Enones

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Summary Highly functionalised branched-chain monosaccharides can be prepared by sensitised irradiation of conjugated enones (**1**) and (**2**) in an alcohol whereupon equatorial 1,4-addition of the carbinol is the major event, the adducts so obtained being correlated with the products of ground-state additions.

1,4-ADDITIONS to the readily available enones (**1**)[1] and (**2**)[2] offer a means of preparing a variety of modified sugars. We report the formation of a number of products arising from photochemical and ground-state 1,4-addition reactions of these enones.

Irradiation† of a solution of enone (**1**) (1·538 g, 8·94 mmol) and benzophenone (0·2553 g, 1·44 mmol) in methanol (720 ml) caused the disappearance of the 215 nm absorption after 5 h. The residue from evaporation showed on t.l.c.

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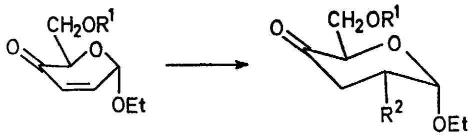
† Irradiations were carried out in a Pyrex vessel in a Rayonet Photochemical Reactor using 'RPR 3500 A lamps' with nitrogen bubbling through the solution.

two new substances in addition to aromatic compounds. Separation by silica column chromatography afforded the major component (**3**) (1·10 g, 65·8%) and a second substance $C_9H_{14}O_5$ (0·237 g, 13·5%) of undetermined structure. In the absence of benzophenone, enone (**1**) was recovered after 5 h irradiation.



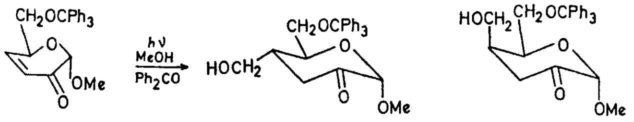
	R^1		R^1	R^2
(**1**)	H	(**3**)	H	CH_2OH
		(**4**)	CPh_3	CH_2OCPh_3
		(**5**)	Ac	CH_2OAc
		(**9**)	H	CMe_2OH
		(**15**)	H	Me
		(**16**)	H	$CH{=}CH_2$
		(**18**)	Ac	Me
(**6**)	Ac	(**7**)	Ac	CH_2OH
		(**11**)	Ac	CHMeOH
(**8**)	CPh_3	(**10**)	CPh_3	CMe_2OH
		(**17**)	CPh_3	CMe

The photoproduct, (**3**) formed a di-*O*-trityl ether (**4**)‡ and a non-crystalline di-*O*-acetate (**5**) characterised as its 2,4-dinitrophenylhydrazone.[4] Diacetate (**5**) could also be obtained by irradiation of the keto-acetate (**6**) in methanol, followed by acetylation of the isolated photoproduct,(**7**). The position and orientation of the newly introduced hydroxymethyl group of (**3**) followed from an n.m.r. doublet at τ 5·0 ($J_{1,2}$ 4·0 Hz) ascribable to 1-H. Under similar conditions, propan-2-ol[3,4] added to (**1**) and to tritylated ketone (**8**) to form the tertiary alcohols (**9**) ($J_{1,2}$ 4·2 Hz) and (**10**) ($J_{1,2}$ 4·0 Hz), respectively. Similarly ethanol added to (**6**) to give the secondary alcohol (**11**) ($J_{1,2}$ 4·0 Hz) characterised as the 2,4-dinitrophenylhydrazone‡ of its methanesulphonate ester. In all cases the yield of the 1,4-photoadduct was 65—85%.

Ground-state additions to ketones (**1**) and (**8**) were studied at −78° using MeMgI, MeLi, and C_2H_3MgBr in the presence of Bu_3PCuI.[5] In all cases there was only one 1,4- addition product (**15**, **16**, or **17**) which showed a coupling constant ($J_{1,2}$ *ca.* 4·0 Hz) consistent with equatorial addition at C-2.

A formal correlation between the products from both sets of 1,4-additions was undertaken. Toluene-*p*-sulphonylation, iodinolysis, and hydrogenolysis of photoproduct (**7**) afforded the same acetate (**18**) obtainable from adduct (**15**).

Irradiation of enone (**2**)[2a] under the conditions described gave two products (**19**) and (**20**) in 65 and 24% yield, respectively, based on unrecovered (**2**). Both products were ketols as shown by their i.r. spectra, and in the light of our experience with enones (**1**), (**6**), and (**8**), we assigned



(2) (19) (20)

the isomeric structures (**19**) and (**20**). In (**19**) a one-proton multiplet at τ 5·9 ascribable to 5-H had $w_{\frac{1}{2}}$ 14 Hz which confirmed the assigned configuration. In contrast, 5-H of (**20**) showed $w_{\frac{1}{2}}$ 6 Hz.

These photochemical and ground-state addition reactions offer efficient methods of introducing branching into the carbohydrate molecule, the products so obtained being suitable for further structural alteration and synthetic manipulation.

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‡ This compound gave correct elemental analysis and spectroscopic data.

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