Photolysis of Carbohydrate Nitro-olefins

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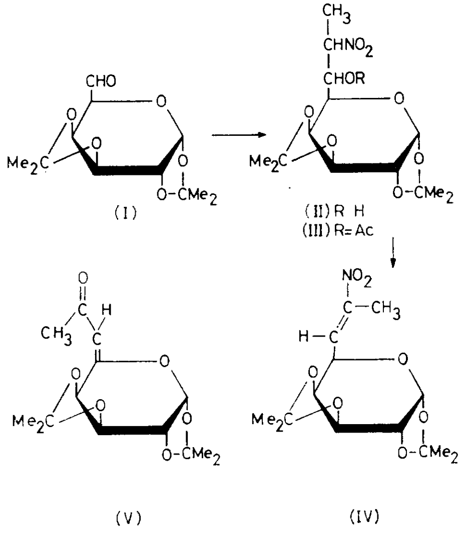
THE photochemistry of nitro-compounds is of interest because of the similarity of their absorption characteristics to those of carbonyl compounds. Some studies of the action of u.v. light on unsaturated nitro-compounds have been described.[1] We report preliminary results of an investigation of the photolysis of unsaturated nitro-sugars.

Addition of nitroethane to 1,2 : 3,4-di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose (I),[2,3] gave a mixture of nitro-alcohols (II) which on acetylation gave three isomers (III). The predominant isomer, m.p. 127—129°, $[\alpha]_D - 73°$ (*c*, 2·4 ethanol), on treatment with triethylamine in benzene,[2] eliminated acetic acid to give *cis*-6,7,8-trideoxy-1,2 : 3,4-di-*O*-isopropylidene-7-*C*-nitro-α-D-*galacto*-oct-6-enose (IV),† m.p. 134—136°, $[\alpha]_D - 109°$ (*c*, 2·6 ethyl acetate), λ_{max} (EtOH) 245 mμ (ε 12,000), and its *trans*-isomer.



Irradiation of (IV) in acetone using a quartz tube with 2537 Å light gave a complex mixture from which three compounds were isolated. One product (27%)‡ was the *trans*-isomer of (IV), m.p. 99—100°, $[\alpha]_D - 90°$ (*c*, 1·1 ethyl acetate), λ_{max} (EtOH) 232 mμ (ε 4700). Structural assignments of the *cis*- and *trans*-isomers are made on the basis of their u.v. and n.m.r. spectra. Molecular models show that there is greater steric hindrance to the attainment of co-planarity of the conjugated system for the *trans*-isomer. The absorption band for this isomer would be expected to occur at shorter wavelength. In the n.m.r. spectra of (IV) and its *trans*-isomer, the signal for the vinyl proton in the *cis*-isomer is at lower field than in the *trans*-isomer: *cis*-isomer τ 5·30(q, H-5, $J_{5,6}$ 8) 2·63(q, H-6, $J_{6,8}$ 1·2 Hz), *trans*-isomer τ 4·95 (br d, H-5, $J_{5,6}$ 7·5) 4·05 (br d, H-6, $J_{6,8} < 1$ Hz).§

The two other products were *cis*- and *trans*-isomers of 6,8-dideoxy-1,2 : 3,4-di-*O*-isopropylidene-α-D-*galacto*-oct-5-enos-7-ulose. The *cis*-isomer (V) (8%) was crystalline and had m.p. 142—143°, $[\alpha]_D - 276°$ (*c*, 0·3 ethyl acetate), λ_{max} (EtOH) 248 mμ (ε 16,000) and τ 4·50 (s, H-6); the *trans*-isomer was a syrup (6%), λ_{max} (EtOH) 256 mμ (ε 11,000) and τ 4·0 (s, H-6). The latter isomer rapidly isomerized to the *cis*-isomer in chloroform at room temperature. The evidence for the structural assignments of the isomers was their u.v. spectra. The formation of the αβ-unsaturated ketones is of particular interest to carbohydrate chemists, because of the resemblance to the Nef reaction, a procedure widely used in monosaccharide synthesis.[4]

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† All new compounds gave elemental analyses, i.r., u.v., and n.m.r. spectra in agreement with the assigned structures.

‡ Values represent yields obtained after extensive purification of photochemical products.

§ N.m.r. spectra were measured in deuteriochloroform at 60 MHz and proton assignments made with aid of spin decoupling.

[1] O. L. Chapman, A. A. Griswold, E. Hoganson, G. Lenz, and J. Reasoner, *Pure Appl. Chem.*, 1964, **9**, 585; O. L. Chapman, P. G. Cleveland, and E. D. Hoganson, *Chem. Comm.*, 1966, 101; J. T. Pinhey and E. Rizzardo, *ibid.*, 1965, 362.

[2] G. B. Howarth, D. G. Lance, W. A. Szarek, and J. K. N. Jones, to be published.

[3] D. Horton, M. Nakadate, and J. M. J. Tronchet, *Carbohydrate Res.*, 1968, **7**, 56.

[4] J. C. Sowden, *Adv. Carbohydrate Chem.*, 1951, **6**, 291.