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Note

Photolysis of deoxyiodo sugars

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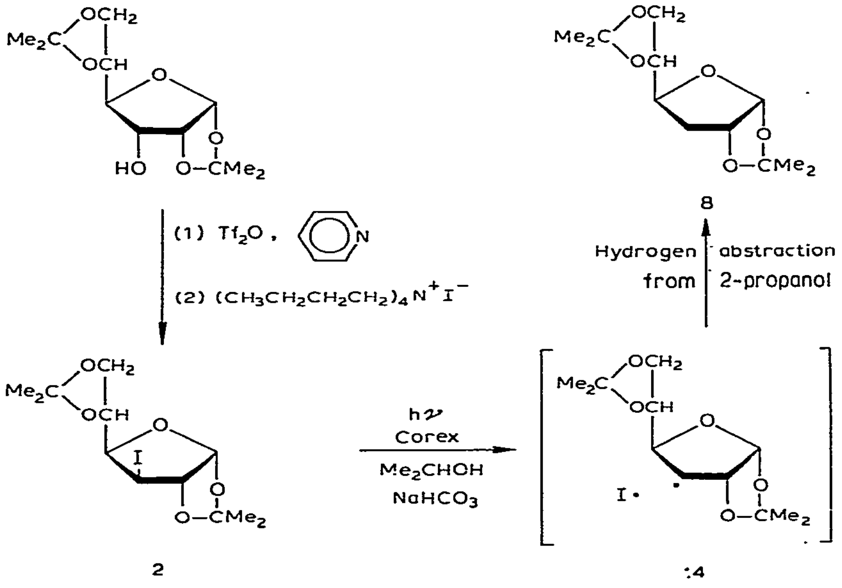
Photolysis of deoxyiodo sugars is one of the mildest methods for conversion of halogenated carbohydrates into deoxy compounds; yet, since the initial report of this reaction over a decade ago[1], there have been only two published examples of its use[2]. Factors that undoubtedly contribute to the infrequent application of this photochemical process include: (*a*) concern about low product-yields and formation of mixtures that are difficult to separate; (*b*) lack of evidence that this reaction is a general one and can be used on a preparative scale; and (*c*) difficulties associated with synthesis of many deoxyiodo compounds. With the development in recent years of several mild, effective reagents for replacement of hydroxyl groups in partially

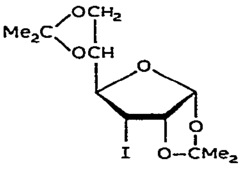
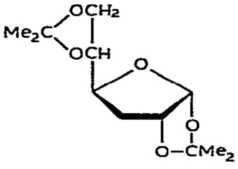
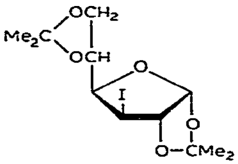
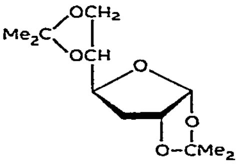
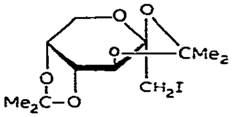
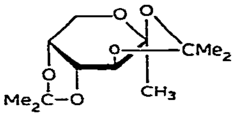
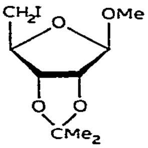
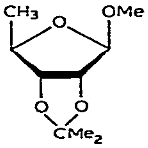
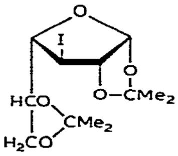
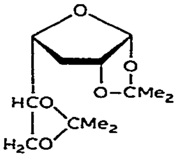
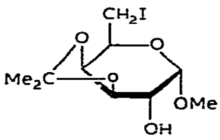
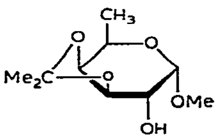
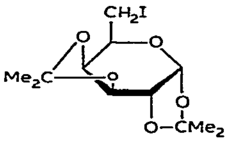
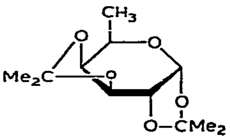


Tf = F_3CSO_2 –

Scheme 1

TABLE I

YIELDS IN PHOTOLYSIS OF IODO DERIVATIVES

Reactant	*Product*	*Yield (%)*	*Ref.*
 1	 8	100	5
 2	 8	99	5
 3	 9	93	6
 4	 10	72	7
 5	 11	90	8
 6	 12	80	9
 7	 13	95	10

protected carbohydrates by iodine (Rydon reagents, triphenylphosphine and carbon tetraiodide, and others)[3], the possibility was raised that the photolysis of iodo compounds could become a useful second step in an extremely mild synthesis of deoxy sugars. This possibility depended upon the photochemical reaction's taking place in high yield and upon its being conducted easily on a synthetically useful scale. The research reported here describes conditions that meet these two criteria.

Compounds **1–7** were prepared from the corresponding partially protected carbohydrates by using the triflate displacement process[4] (Scheme 1). Corex-filtered irradiation of each of these iodides (**1–7**) in 2-propanol in the presence of sodium hydrogencarbonate under a nitrogen atmosphere resulted in formation of the corresponding deoxy compounds **8–13** in the yields shown in Table I. Product isolation was simple; it consisted of distillation of the 2-propanol, extraction of the carbohydrate-containing material from the residue with ethyl ether, and distillation of the ethyl ether. Chromatography or distillation of products was unnecessary.

Each of the iodides **1–7** required 3 h of irradiation to convert 2 g of material. To determine whether the product yield would decrease when the quantity of material irradiated was increased, a 10-g sample of **7** (and 5 g of sodium hydrogencarbonate) was photolyzed until the starting material was totally consumed (15 h). The percent yield was the same (95%) as that obtained for the 2-g sample (Table I).

Selection of reaction conditions for iodide photolysis may have a dramatic effect upon product yield and reaction-mixture complexity. Reaction of 3-deoxy-3-iodo-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**2**) provides an example of this effect. Irradiation of **2** in methanol using unfiltered light from a mercury lamp results in formation of a mixture of products from which 3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranose (**8**) was isolated in 32% yield after chromatography[2b]. In contrast, when 2-propanol is used as the reaction solvent and the incident light is passed through a Corex filter (transparent at wavelengths longer than 260 nm), **8** is formed in 99% yield (Table I). Chromatography is not necessary. The effect of these changes in reaction conditions on product yield is understandable. 2-Propanol is a better solvent than methanol for the photochemical reaction, as it is a better hydrogen-atom donor and, consequently, allows more-facile hydrogen-abstraction from the solvent by such photochemically generated radicals as **14** (Scheme 1). Also, irradiation with light of much greater energy than that necessary to cause homolytic cleavage of the carbon–iodine bond (namely, unfiltered light) opens new reaction-pathways and, thus, allows the possibility for more-complex mixtures of products. This type of dependence of product yield and reaction-mixture complexity on excitation wavelength has been observed during irradiation of **7**, the only iodide in Table I (other than **2**) whose photolysis has previously been reported[1].

In conclusion, the results from this study show that the photochemical reaction of deoxyiodo sugars provides a simple and effective second step in a pathway for synthesis of deoxy sugars from the corresponding hydroxyl compounds.

EXPERIMENTAL

General methods. — ^{1}H-N.m.r. spectra were obtained with a Varian T-60 spectrometer by using carbon tetrachloride as the solvent. Mass spectra were recorded with a Finnigan 1015-D mass spectrometer, using electron impact with an ionizing voltage of 70 eV.

Irradiation procedure. — Each of the iodides **1–7** was photolyzed as follows.

The deoxyiodo sugar (2.0 g) and sodium hydrogencarbonate (1.0 g) were dissolved in 2-propanol (350 mL) and placed in a photochemical reaction-vessel. A water-cooled, quartz immersion-well containing a 450-W, medium-pressure, mercury-vapor lamp was lowered into the reaction vessel, and a Corex filter was inserted between the light source and the mixture. The reaction vessel, was purged with nitrogen for 2 h prior to irradiation and the purge was continued during the 3 h of irradiation. After photolysis, the 2-propanol was distilled off *in vacuo* below 30°, and the resulting residue extracted with three 50-mL portions of ethyl ether. The ether extracts were combined and the ether evaporated to leave the corresponding deoxy sugar. The yields of the deoxy sugars from photolysis of **1–7** are given in Table I. Each photoproduct was identified by comparison of mass and ^{1}H-n.m.r. spectra with those obtained from authentic samples. References to the procedures used to synthesize the authentic samples are given in Table I.

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