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Preliminary communication

A new oxidation process for partially protected carbohydrates

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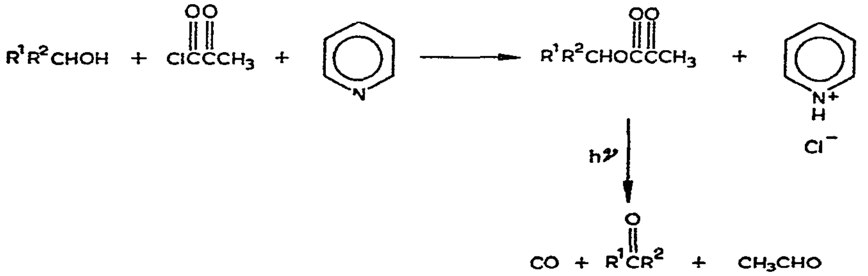
This communication describes a new process for the oxidation of hydroxyl groups in carbohydrate systems to carbonyl groups. This process consists of formation of the pyruvic ester of the alcohol to be oxidized, followed by photochemical reaction of this ester[*]. Results from a study of five compounds selected to test this oxidation sequence reveal the following features: (*a*) product yields are good (Table I); (*b*) primary and secondary alcohols are oxidized with equal ease, (*c*) the process is conducted under mild conditions, that is, at room temperature or below in an inert solvent and in the absence of acids or inorganic ions, and (*d*) the photochemical step is rapid and not complicated by competing reactions. Described here is the procedure for conducting the pyruvate oxidation-process and a brief comparison of pyruvate oxidation to existing methods.



Oxidation of each of five alcohols, 1,2 5,6-di-*O*-isopropylidene-α-D-glucofuranose[†] (**1**), 1,2 4,5-di-*O*-isopropylidene-β-D-fructopyranose[2] (**2**), 2,3 4,5-di-*O*-isopropylidene-β-D-fructopyranose[2] (**3**), 1,2 3,4-di-*O*-isopropylidene-α-D-galactopyranose[3] (**4**), and methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside[4] (**5**), was conducted in the same manner. The acid chloride of pyruvic acid[5] in benzene was added slowly at 25° to a stirred benzene solution of one equivalent of the appropriate alcohol and of pyridine. Ester formation was immediate and quantitative. The pyridinium hydrochloride was removed by filtration and the ester (20 mM) in benzene subjected to Pyrex-filtered irradiation under nitrogen with a 450-W Hanovia, medium pressure, mercury lamp. (In

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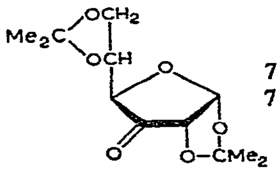
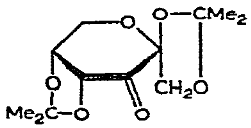
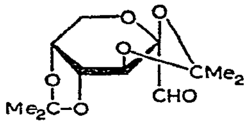
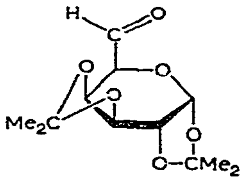
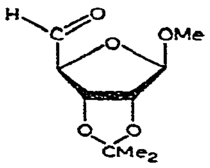
[*] The photochemical reactions of three pyruvic esters (methyl, ethyl, and 2-propyl) have been reported, see Ref. 1.

[†] Pfanstiehl Laboratories, Inc., Waukegan, Illinois.

TABLE I

OXIDATION OF ALCOHOLS 1–5

Alcohol	*Oxidation products*	*Percent yields*			
		Pyruvate oxidation	*Chromium trioxide in pyridine*	*Ruthenium tetraoxide*	*Me_2SO based reagents*
1	 6	71[a] 74[b]	6[c] 0[f]	75–95[d]	45–65 (P_2O_5)[e] 0–70 (DCC)[g] 62 (Ac_2O)[h]
2	 7	53[i] 57[b]		55–75[j]	52–70 (Ac_2O)[k]
3	 8	62	53[f]	[m]	84 (DCC)[n]
4	 9	70	62[f]		46–83 (DCC)[o] Low (Ac_2O)[p]
5	 10	65	75[f]	Low[q]	48–80 (DCC)[r]

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[a] 14% recovery of alcohol 1. [b] Reaction mixture subjected to re-oxidation. [c] See ref. 6. [d] See refs. 7–11. [e] See refs. 12–14. [f] See ref 21 [g] See refs. 13 and 15. [h] See ref 16. [i] 13% recovery of alcohol 2. [j] See ref. 17. [k] See refs. 17–20. [m] See ref. 19 [n] See ref. 22. [o] See refs. 23–26 [p] See ref 27. [q] See ref. 28. [r] See refs. 13 and 28.

initial syntheses, each ester was isolated and characterized; however, isolation was not essential for the oxidation process.) In general, irradiation for 45 min was sufficient for conversion of one gram of ester. In each instance, removal of benzene at 25° yielded a light-yellow oil that was distilled (simple distillation) to give colorless material. The distillates from oxidation of compounds 3, 4, and 5 were homogeneous and were identified as aldehydes 8, 9, and 10, respectively (Table I), initially by instrumental techniques (n.m r , i r , and g.l c.–m s) and ultimately by comparison with known samples. The distillates from reactions of alcohols 1 and 2 contained mainly the ketones 6 and 7, respectively, with minor amounts of the corresponding starting alcohols (1 and 2, Table I). The presence of these alcohols was diminished to a low level (2–4%) and yields of carbonyl compounds 6 and 7 slightly increased by subjecting the entire mixtures again to the oxidation process (Table I). The yields reported in Table I are calculated from the amount of product isolated after distillation. N m r spectra of reaction mixtures before and after distillation showed only minor differences

Analysis of the data in Table I reveals that pyruvate oxidation is an effective method for oxidizing compounds 1–5. Only the dimethyl sulfoxide based reagents are comparable in versatility to pyruvate oxidation, however, the product yields from Me_2SO-based reagents vary considerably, depending upon the compound (P_2O_5, *N,N'*-dicyclohexylcarbodiimide, Ac_2O, or other reagents) accompanying dimethyl sulfoxide in the mixture Thus, this new photochemical technique compares favorably in product yield and versatility to the most widely used oxidizing agents in carbohydrate chemistry.

None of the five systems studied (1–5) provides an adequate test of the efficacity of pyruvate oxidation when extremely sensitive alcohols or carbonyl compounds are involved; this aspect requires further study.

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