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Deuterium Isotope Effect and Oxidation of Labelled Alcohols

Short Communication

Manouchehr Saljoughian

School of Pharmacy, Isfahan University, Isfahan, Iran

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Oxidation of alcohols *R*—CHD—OH by CrO_3/pyridine gave the aldehydes *R*—CDO with a relatively small loss of D thus indicating a pronounced isotope effect.

[Keywords: Aldehydes, D *labelled;* H—D *Isotope effect; Tris(triphenyl-phosphine) ruthenium dichloride]*

Deuterium-Isotopeneffekt bei der Oxidation von markierten Alkoholen (Kurze Mitteilung)

Die Oxidation von Alkoholen *R*—CHD—OH mit CrO_3/Pyridin ergab die Aldehyde *R*—CDO, wobei auf Grund eines ausgeprägten Isotopeneffekts der Verlust von D verhältnismäßig gering blieb.

In the course of experiments on the synthesis of partially deuterated compounds, some deuterium isotope effects were observed, when labelled alcohols were oxidized to the corresponding aldehydes. As C_6H_5—CH_2OD was heated to 200° for 45 min in the presence of 40 mg tris(triphenyl-phosphine) ruthenium dichloride, the deuterium bond to the oxygen was exchanged exclusively with the hydrogen atom at the C-1 carbon atom. The advantages of this procedure for isotopic labelling of primary alcohols in the C-1 position are its simplicity, low cost, avoidance of reactive oxidants and reductants, and the ability of the exchange to be carried out under neutral *pH*[1,2]. On the other hand only 8% deuterium of the alcohol (originally 51%) was lost during its oxidation to the corresponding aldehyde (43%) by a complex of CrO_3 and pyridine in CH_2Cl_2. The same results were obtained when (1-^2H)

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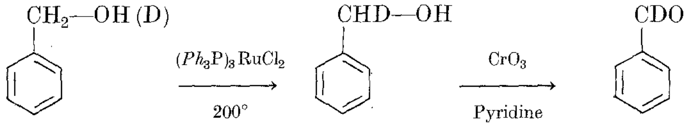
cinnamyl alcohol and (1-^{2}H) crotonic alcohol were oxidized to (1-^{2}H) cinnamaldehyde and (1-^{2}H) crotonaldehyde respectively. The results are shown in the table.

Alcohols Hydroxy labelled	Alcohols (C-1 labelled)	%D	Aldehydes (C-1 labelled)
C_6H_5—CH_2OH (D)	C_6H_5—CHD—OH	51	C_6H_5—CDO
C_6H_5—CH=CH—CH_2OH (D)	C_6H_5—CH=CH—CHD—OH	48	C_6H_5—CH=CH—CDO
CH_3—CH=CH—CH_2OH (D)	CH_3—CH=CH—CHD—OH	46	CH_3—CH=CH—CDO

These data indicate that during oxidation of the alcohols the C—D bond is less affected than the C—H bond thus showing obviously a deuterium isotope effect. These findings are also useful in order to save the stable isotope during the experiments[3].

Experimental

For nmr analysis the deuteriated and non-deuteriated compounds (10 mg, in separated nmr tubes) were accurately weighed and dissolved in $CDCl_3$ (5 ml) and a trace of TMS was added as reference[3]. To ascertain the percent of deuterium incorporation the intensity of the corresponding nmr peaks in the labelled and non-labelled spectra were accurately determined (spectrometer: Varian T-60 A).



Preparation of (methylene-^{2}H) benzyl alcohol

Benzyl alcohol (2 g) was mixed with tris(triphenyl phosphine)ruthenium dichloride (40 mg) and deuteriated water (0.5 ml) in a sealed tube and heated for 45 min at 200 °C. The tube was cooled and opened. The deuteriated alcohol was dried ($MgSO_4$) and distilled. Yield 1.25 g, b.p. 93°/11 mm.

Oxidation of (methylene-^{2}H) benzyl alcohol

(Methylene-^{2}H)-benzyl alcohol (10 mmol) was oxidized at room temperature for 15 min with a complex of CrO_3/pyridine in methylene chloride under N_2; the product was the corresponding aldehyde[4]. Yield 90% b.p. 64°/10 mm. The same procedure was carried out likewise for all other compounds.

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