EFFICIENT METHOD FOR THE HYDROLYSIS OF 4-CHLOROTETRAHYDROPYRANS

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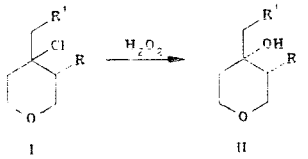
It is known that 4-chlorotetrahydropyrans I and a number of other compounds that contain a chlorine atom attached to a tertiary carbon atom undergo primarily dehydrochlorination (no less than 60-70%) when attempts are made to hydrolyze them under the influence of dilute aqueous solutions of bases or acids [1].

We have shown that when hydrolysis is realized by means of hydrogen peroxide, the dehydrochlorination of 4-chlorotetrahydropyrans I can be suppressed, and tetrahydropyranols II can be obtained in high yields (63-85%).



I II

I, II a $R=R^1=H$; b $R=CH_2OCH_3$, $R^1=H$; c $R=H$, $R^1=CH_2OCH_3$

As expected [2], tertiary alkyl chlorides under these conditions form hydroperoxides that do not undergo further changes under the reaction conditions.

The structures of the compounds obtained were proved by the PMR spectra, as well as by identification with known samples [by gas-liquid chromatography (GLC)].

A mixture of 0.1 mole of chloride I and 0.2 mole of 30% of hydrogen peroxide was stirred at 50-60° for 16-24 h to give pyranols IIa-c.

Compound IIa. This compound was obtained in 63% yield and had bp 81-83°C (12 mm) and n_D^{20} 1.4420.

Compound IIb. This compound was obtained in 69% yield and had bp 121-122°C (12 mm), n_D^{20} 1.4710, and d_4^{20} 1.0732. PMR spectrum (CCl_4): 1.12 and 1.26 (3H, s, CH_3), 1.43-2.05 (3H, m, CH_2 and CH), 3.31 (3H, s, OCH_3), 3.4-3.8 (6H, m, OCH_2), and 4.02 ppm (1H, s, OH).

Compound IIc. This compound was obtained in 85% yield and had bp 128-129°C (12 mm), n_D^{20} 1.4695, and d_4^{20} 1.0643. PMR spectrum (CCl_4): 1.35-1.75 (6H, m, CH_2), 3.29 (3H, s, OCH_3), 3.46-3.84 (6H, m, OCH_2), and 4.14 ppm (1H, s, OH).

LITERATURE CITED

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