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Convenient Preparation of Acetals over Hydrous Zirconium Oxide

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(Received October 17, 1989)

Synopsis. Aldehydes and ketones were efficiently converted to the corresponding acetals by the reaction with ethylene glycol over hydrous zirconium oxide. The reaction could proceed under reflux condition or at room temperature. The compound, which was unstable in acid, was also acetalized by this catalyst.

Acetalization of carbonyl compounds is generally carried out under homogeneous condition and strong acid is used as a catalyst. Although these methods have several benefits, it was rather troublesome to remove the acid catalyst after acetalization, and the application is difficult for the compounds which are unstable in acids.

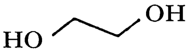
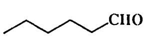
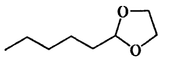
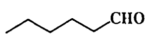
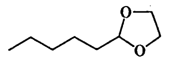
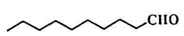
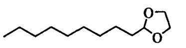
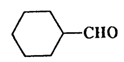
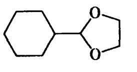
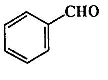
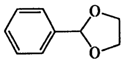
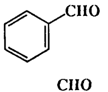
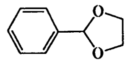
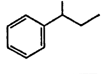
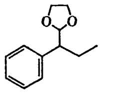
In the previous papers, we reported that the reduction of aldehydes or ketones with 2-propanol over hydrous zirconium oxide proceeds efficiently to give the corresponding alcohols, and that the reaction of hexanal with methanol or ethanol gives mainly dimethoxy or diethoxy acetal, respectively.[1] In this paper, we report that carbonyl compounds are easily acetalized with ethylene glycol over hydrous zirconium oxide. This method has the following advantages; 1) the oxide is not soluble to any solvent, and the catalyst can be easily removed by filtration, 2) the oxide is stable at room temperature in air over 7 years, and can be used for repeated reactions, 3) the oxide is not sensitive to air or water, and the reaction does not need water free conditions, 4) the reaction can proceed efficiently without azeotropic removal of water, 5) the oxide does not have strong acidic sites, therefore the acetalization can apply for compounds which are unstable in acids.

Experimental

Hydrous Zirconium Oxide. To a solution of zirconium(IV) dichloride oxide ($ZrOCl_2 \cdot 8H_2O$) (200 g of solid in 10 dm^3 deionized water) an aqueous solution of sodium hydroxide (1 mol dm^{-3}) was slowly added at room temperature. Constant gentle stirring was maintained and the addition was continued until the pH of the resulting solution reached 6.80. The solution was allowed to stand for 48 h at room temperature. The resulting product was filtered and washed free from chloride ions. The gel was spread on a glass plate and dried in air at room temperature for 10 h and at 80 °C for 2 h. Fifty four grams of hydrous zirconium oxide was obtained in the form of granules, and was heated at 300 °C for 5 h.

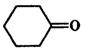
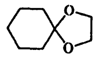
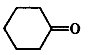
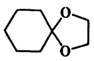
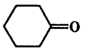
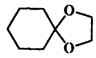
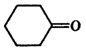
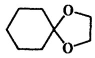
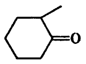
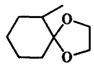
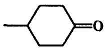
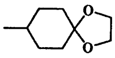
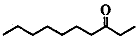
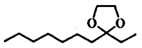
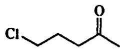
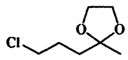
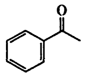
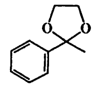
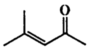
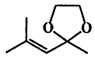
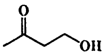
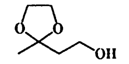
Acetalization. In a 50 cm^3 round-bottom flask equipped with a reflux condenser was placed hydrous zirconium oxide (24—60 mesh; 1.0 g), an aldehyde or ketone (5 mmol), ethylene glycol (5 or 10 mmol), and a hydrocarbon (0.5 mmol) as an internal standard. The reactions were carried out under the following three conditions; A) benzene (10 cm^3) was used as solvent, and the reactions were carried out under gentle reflux for 4 h, B) benzene (10 cm^3) was used as solvent and the reactions were carried out under gentle reflux with azeotropic removal of water for 1 h, C) tetrahy-

Table 1. The Reaction of Aldehydes with Ethylene Glycol over Hydrous Zirconium Oxide[a]

Entry	Aldehyde	Condition[b]	 mmol	Product	Yield %
1		A	5		90
2		C	10		65
3		A	10		92
4		A	10		98
5		A	10		72
6		B	10		80
7		A	10		80

a) Aldehyde; 5 mmol; catalyst; 1.0 g, solvent; 10 cm^3. b) Condition A: solvent; benzene, reflux for 4 h, Condition B: solvent; benzene, reflux with azeotropic removal of water for 1 h, Condition C: solvent; tetrahydrofuran, at room temperature for 20 h.

Table 2. The Reaction of Ketones with Ethylene Glycol over Hydrous Zirconium Oxide[a)]

Entry	Ketone	Condition[b)]	$HOCH_2CH_2OH$ mmol	Product	Yield %
1		A	5		74
2		A	10		90
3		B	5		83
4		C	10		72
5		C	10		31
6		C	10		79
7		A	5		32
8		A	5		80
9		A	10		30
10		A	10		15
11		C	10		28

a) Ketone; 5 mmol, catalyst; 1.0 g, solvent; 10 cm^3. b) Condition A: solvent; benzene, reflux for 4 h, Condition B: solvent; benzene, reflux with azeotropic removal of water for 1 h, Condition C: solvent; tetrahydrofuran, at room temperature for 20 h.

drofuran (10 cm^3) was used as solvent and the reactions were carried out at room temperature for 20 h. The concentration of the products was analyzed by GLC (a capillary column PEG 20M 30 m). The identification of the products was made by comparison of retention times in GLC with those of authentic samples.

Results and Discussion

Most of the aldehydes and ketones were efficiently converted to the corresponding acetals over hydrous zirconium oxide. They are listed in Table 1 and Table 2. As shown in Entries 5 and 6 of Table 1 and in entries 1 and 3 of Table 2, benzaldehyde and cyclohexanone were efficiently acetalized under both conditions with and without azeotropic removal of water. These results suggested that the acetalization could be achieved conveniently with only reflux. The ratio of ethylene glycol to the carbonyl compound slightly effected the acetalization rate (Entries 1 and 2 of Table 2). It is notable that the acetalization could proceed at room temperature.

The acetalization rate of 2-methylcyclohexanone was slower than that of cyclohexanone or 4-methylcyclohexanone (Entries 4, 5, and 6 in Table 2). This was explained by steric hinderance. The acetalization of an α,β-unsaturated ketone was difficult compared with that of a saturated ketone (Entry 10 of Table 2). The most valuable result was found in the acetalization of 4-hydroxy-2-butanone. Generally, the reaction of this compound with an acid catalyst mainly caused dehydration to give methyl vinyl ketone. Because of low acidity of hydrous zirconium oxide,[2)] the dehydration was suppressed and the acetalization mainly proceeded at room temperature (Entry 11 of Table 2).

References

1) M. Shibagaki, K. Takahashi, and H. Matsushita, *Bull. Chem. Soc. Jpn.*, **61**, 3283 (1988); M. Shibagaki, H. Kuno, K. Takahashi, and H. Matsushita, *ibid.*, **61**, 4153 (1988); M. Shibagaki, K. Takahashi, H. Kuno, H. Kawakami, and H. Matsushita, *Chem. Lett.*, **1988**, 1633.

2) M. Shibagaki, K. Takahashi, H. Kuno, and H. Matsushita, *Bull. Chem. Soc. Jpn.*, **63**, 258 (1990).