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M. Narayana Rao [a] , Pradeep Kumar [a] , Anand P. Singh [a] & Ravinder S. Reddy [a]
[a] National Chemical Laboratory , Pune, 411 008, India

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A CONVENIENT METHOD FOR THE CLEAVAGE OF ACETALS USING ZEOLITES[#]

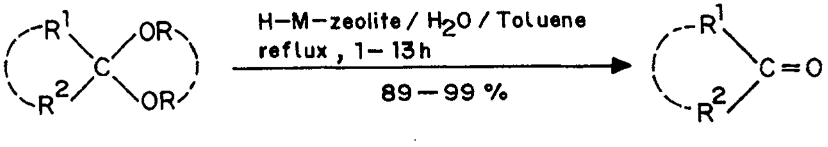
M. Narayana Rao[*], Pradeep Kumar, Anand P. Singh and Ravinder S. Reddy
National Chemical Laboratory, Pune 411 008, India

Abstract: Cleavage of acetals and ketals with H-mordenite zeolite afforded carbonyl compounds in excellent yields.

The catalytic potential of zeolites in organic synthesis is becoming increasingly important for a wide range of reactions.[1-3] The acid and base properties of zeolites, which can be altered by the exchange of cations, have made them versatile catalysts.[4] Although the commercial silica-alumina cracking catalysts, the cation exchanged Y type, and H-ZSM-5 zeolites have been used for the preparation of acetals,[5,6] however, their potential in the cleavage of acetals has not been fully utilized. In this communication, we describe a convenient liquid phase cleavage of acetals and ketals using H-mordenite (H-M) zeolite (Si/Al = 9.62).[7].

The conversion of acetals to carbonyl compounds is often a useful and necessary organic transformation. So far a number of catalysts, e.g. acids,[8] Lewis acids,[9] sodium hydrogen telluride,[10] silica gel,[11] ferric chloride on silica gel,[12] and amberlyst-15,[13] have been developed for this purpose. Our deprotection method with H-M-zeolite, where the change is from a conventional homogeneous to heterogeneous procedure, brings advantages in respect of easy separation, higher and consistent yields, and regeneration of the catalyst. Further, the presence of the required BrØnsted and Lewis acid centers in the H-M-zeolite itself, in contrast to silica gel which required an external acid (oxalic or sulphuric) along with it for consistent yields,[11] extends significantly the scope of this method.

Hydrolysis of acetals and ketals **1a-m** catalyzed by H-M-zeolite afforded the carbonyl compounds **2a-m** in excellent yields (Table). The work-up is exceedingly simple, only involving the filtration of the zeolite and removal of solvent to obtain the product in a high state of purity. In general, the reaction was monitored by gas chromatography by removing aliquots from



1a–m

2a–m

the reaction. The zeolite can be reactivated for reuse by heating at 500° C under air.

The results shown in the Table demonstrate that a wide range of acetals and ketals of carbonyl compounds, including saturated (**1e-i,k,l**) and a,ß-unsaturated (**1c**) aliphatic, aromatic (**1a,d,j,m**) and heteroaromatic (**1b**) compounds, may be cleaved in this manner. The catalyst is equally effective for both cyclic (**1d-f,h-m**) as well as acyclic (**1a-c,g**) acetals and ketals. Further, the vinyl ethers and neopentylalkanals, which selectively formed in the vapour phase reaction of acyclic acetals and cyclic acetals of neopentyl glycol, respectively with zeolites,[3] were not detected in this liquid phase method.

The hydrolysis of acetals with H-M-zeolite (1-13 h, Table) was slow compared to ion exchange resin, amberlyst-15[13] due to its lower acidity. This may offer the potential of selective deprotection. Thus, the ketals (**1g-m**) were hydrolyzed faster than acetals

Table: Hydrolysis of acetals with H-M-zeolite

Acetal	R, R	R^1, R^2	Time	Product[a]	Yield[b] (%)
1a	Et, Et	Ph, H	9 h	**2a**	89
1b	Et, Et	2-furyl, H	8 h	**2b**	96
1c	Et, Et	$CH_3CH=CH$, H	10 h	**2c**	95
1d	CH_2CH_2	Ph, H	12 h	**2d**	90
1e	CH_2CH_2	$CH_3(CH_2)_2$,H	8 h	**2e**	89[c]
1f	CH_2CH_2	$CH_3(CH_2)_8$,H	13 h	**2f**	90
1g	Et, Et	$(CH_2)_5$	3 h	**2g**	98
1h	CH_2CH_2	$(CH_2)_5$	5 h	**2h**	97
1i	CH_2CH_2	Et, CH_3	3 h	**2i**	95[c]
1j	CH_2CH_2	Ph, CH_3	3 h	**2j**	99
1k	CH_2CH_2	d	3 h	**2k**	98
1l	$CH_2C(CH_3)_2CH_2$	d	1 h	**2l**	99
1m	$CH_2C(Et)_2CH_2$	e	1 h	**2m**	96

[a] All products exhibit IR and ^{1}H NMR spectral data in accord with those of corresponding authentic samples. [b] Yield of isolated product. [c] Reaction is performed in dichloromethane at reflux temperature. [d] (-)-menthone. [e] a-tetralone.

(**1a-f**, Table). Further, the faster hydrolysis of 5,5-dimethyl-1,3-dioxane (**1l**) compared to 1,3-dioxolane (**1k**) is in accordance with the earlier observation with mineral acid.[14]

The superiority of H-M-zeolite over conventional silica gel can be seen from the reaction of acetal **1d** and ketal **1h**. These compounds were recovered unreacted even after refluxing for 12 h with silica gel (Merck, 230-400 mesh) compared to the formation of the carbonyl compounds **2d** and **2h** with zeolite in 90% and 97% yields respectively (Table). Other zeolites, H-ZSM-5 and molecular sieves 5A, were found to be ineffective in the cleavage of acetals and ketals.

In conclusion, from commercially available zeolite we have established a convenient heterogeneous catalytic method for the cleavage of acetals. Further, the suitable acidity of H-M-zeolite effects the reaction in high and consistent yields.

Experimental

Acetals were prepared from the corresponding carbonyl compounds according to the literature procedure[8]. H-M-Zeolite was a gift sample from Laporte Inorganic, U.K. The unit cell composition of this H-M-zeolite is $H_{4.52}(AlO_2)_{4.52}(SiO_2)_{43.48}O_{96}\cdot 24\ H_2O$.

Hydrolysis of Acetals and ketals with H-M-zeolite; General Procedure:

To a solution of the acetal **1** (10 mmol) in toluene (5 ml) containing water (1 ml) was added H-mordenite zeolite (0.6 g). The mixture was refluxed with stirring (magnetic stirbar) and the progress of the reaction was followed by GC analysis (OV-101 column). When the reaction was complete, the zeolite was filtered and the filtrate was concentrated to afford the carbonyl compound **2** (Table).

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