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THIOACETALIZATION OF CARBONYL COMPOUNDS BY ZEOLITE HSZ-360 AS A NEW, EFFECTIVE HETEROGENEOUS CATALYST

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Abstract: Thioacetal can be efficiently obtained at room temperature by simply dissolving the appropriate carbonyl compounds and 1,2-ethanedithiol, in dichloromethane, with zeolite HSZ-360 as a new heterogeneous catalyst. Satisfactory to good yields are obtained even with polyfunctionalized substrates.

Thioacetalization of carbonyl compounds plays an important role in organic synthesis since the thioacetal group acts as a protecting group or as an acyl anion equivalent.[1,2] Dithioacetals are generally obtained by protic or Lewis acid catalyzed condensation of carbonyl compounds with thiols.[1,3] However, many of these methods suffer from harsh conditions, expensive reagents or corrosive catalysts.

The development and application of efficient heterogeneous catalysts performing chemical transformations has received great interest mainly due to the easier work-up with economical and, frequently, advantages for industrial processes.[4] In this context, different environmentally friendly conditions have been

Table. Reaction of carbonyl compounds with 1,2-ethanedithiol.

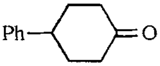
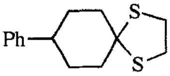
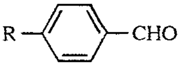
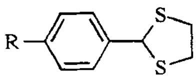
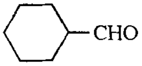
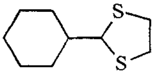
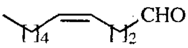
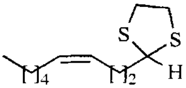
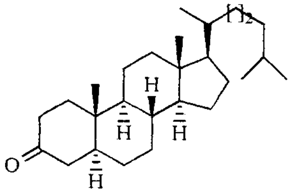
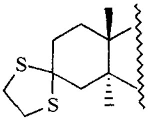
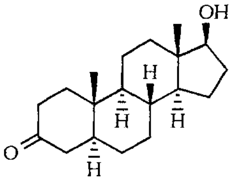
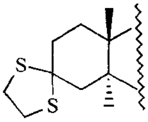
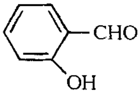
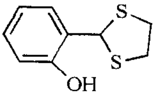
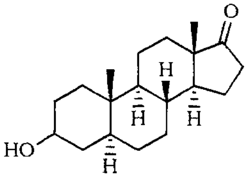
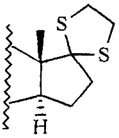
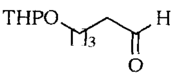
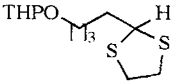
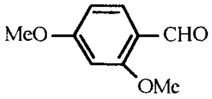
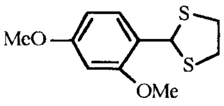
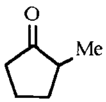
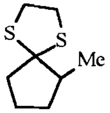
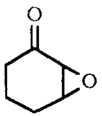
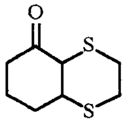
	Substrate **1**	Product **2**	Yield (%)
a			100^a
b-e		 **b** R=Ph **c** R=CN **d** R=MeO **e** R=NO_2	88^a 87^a 65^a 85^a
f			100^a
g			94^a
h			100^a
i			100^a
j			75^b
k			60^a
l			65^a

Table. (Contd...

	Substrate **1**	Product **2**	Yield (%)
m			95[b]
n			85[a]
o			82[b]

[a]Reaction time 15h. [b]Reaction time 40h.

reported for the preparation of the title compounds, these include Amberlyst-15,[5] bentonitic earth,[6] *bis*(trimethylsilyl)sulfate-silica,[7] cobalt(II) bromide-silica gel,[8] Envirocat EPZG®,[9] Fe^{3+}-montmorillonite,[10] natural kaolinitic Clay,[11] and zirconium(IV) chloride-silica gel.[12] Nevertheless, some of these require preparation and/or activation of the catalyst,[6,7,9,10,12] dry conditions,[6,8,12] the use of hazardous solvents at reflux temperature,[5,9,11] or are effective only for aldehydes.[10]

Zeolite catalysts have received considerable attention in the last decade due to their characteristic properties such as shape selectivity, thermal stability, acidic and basic nature.[13] H-Y Zeolite (Si/Al = 2.43) has been reported to be effective[14] for the dithioacetalization, however, this catalyst must be activated at 500 °C prior to use, and reflux temperature is needed.

During our study devoted to the utilization of zeolites in organic synthesis,[15] we have now found that HSZ-360, a commercial dealuminated Y-Zeolite (Tosoh Corporation),[16,17] can be conveniently used for the thioacetalization of carbonyl compounds, under mild conditions.

The preparation of the title compounds[18] is carried out at room temperature by mixing 10 mmol of carbonyl compound and 12 mmol of ethanedithiol in dichloromethane and in the presence of 300 mg of zeolite HSZ-360 (utilized without previous thermal or chemical treatment). Satisfactory to high yields (60-100%, see Table) are obtained even with steroidal ketones and aromatic aldehydes possessing electron-withdrawing or electron releasing group. No reaction is observed when benzophenone is used as starting substrate. Anyhow, this method is mild enough to preserve other functionalities such as (*Z*)-double bond, nitro, cyano, tetrahydropyranyl, and ethers. However, a carbonyl compound containing an epoxy moiety afforded completely different product due to the preferential attack of ethaneditiol on the epoxy group (entry **o**).

In conclusion, we have shown an efficient, mild and selective synthesis of thioacetals from carbonyl compounds and 1,2-ethanedithiol promoted by commercial Zeolite HSZ-360.

General Reaction Procedure - To a stirred solution of carbonyl compound (10.0 mmol) and 1,2-ethanedithiol (12.0 mmol) in CH_2Cl_2 (30 ml), HSZ-360 (300 mg) was added. The mixture was stirred for the appropriate time (see Table 1) at r.t. Upon completion of the reaction, checked by GC or TLC, the mixture was filtered and the residue was washed with CH_2Cl_2. The filtrate was washed with 2N aqueous sodium hydroxide (3 x 20 ml) to remove the excess dithiol. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to afford the product, generally pure. However, when necessary, the dithioacetals can be purified by flash chromatography.

Analytical data for the product **2o**: IR ($CHCl_3$): ν = 1717 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.55-2.22 (4H, m), 2.42-2.68 (2H, m), 2.72-3.23 (5H, m), 3.85 (1H, bd, *J* = 10.8 Hz, COCHS). ^{13}C NMR (50.289 MHz, $CDCl_3$): δ = 25.8, 30.9, 31.3, 32.3, 42.2, 47.7, 59.5, 204.7. MS *m/z* (70 eV): 188 [M^+], 160, 144, 128, 118, 105 (100%), 97, 85, 67, 55. Anal. Calcd. for $C_8H_{12}OS_2$: C, 51.03; H, 6.42; S, 34.05. Found: C, 50.97; H, 6.51; S, 34.13

Acknowledgements

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(16) Surface area 500±10 m^2/g, determined in our laboratory by B.E.T. method: Brunauer, S.; Emmett , P. H. and Teller, E. *J. Am. Chem. Soc.* **1938**, *60,* 309.

(17) SiO_2/Al_2O_3 ratio 14.0 and pore dimension 7.4 Å, Surface acidity 0.51±0.03 med. H^+/g: determined in our laboratory by programmed desorption of ammonia gas (NH_3-TPD), Berteau, P. and Delmon, B. *Catal. Today* **1989**, 5, 121.

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