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Selective Oxidation of Diols by H_2O_2/TS-1 System and by DMDO.

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Abstract: Selective oxidations of secondary hydroxyl groups vs. primary ones in 1,n-diols by TS-1/H_2O_2 catalitic system and by dimethyldioxirane, new reagents with low environmental pollution, are reported.

The achievement of new methodologies to selectively transform functional groups with similar reactivity, is a major topic of several groups of researchers. One of these targets is, in example, the selective oxidation of diols.

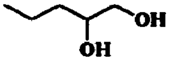
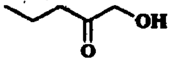
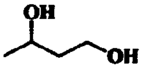
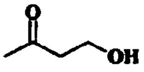
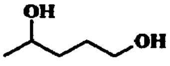
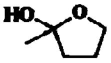
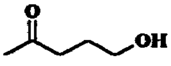
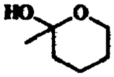
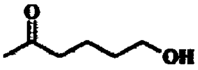
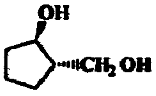
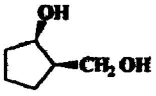
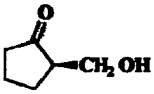
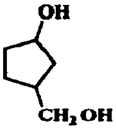
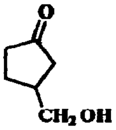
Many oxidizing agents are known to convert alcohols into carbonyl compounds. The majority of synthetic methods, reported in literature, still utilize metal species,[1] with chromium compounds being employed in the largest part. Also non metal oxidants, such as DMSO-based reagents,[2] are well known and often used. However, only few methods[3] show a good selectivity towards secondary alcohols, while many others work poorly with saturated linear,[4] or cyclic[5] diols. Moreover their polluting byproducts represent a significant limitation to their use.

As for metal-catalyzed H_2O_2 oxidations of alcohols,[6] the preparative value of this procedure is, in some instances, limited, especially when high H_2O_2 concentrations are required.

In the last years, we have concentrated attention on efficient oxidation reagents with minimal environmental impact, mainly H_2O_2/TS-1 system and dimethyldioxirane (DMDO).

The catalytic system H_2O_2/TS-1 showed to be of peculiar interest. TS-1 is a metal doped zeolite in which certain silicon atoms were substituted with titanium ones; it gives rise to a hydroperoxidic species in presence of hydrogen peroxide; the substrate is then adsorbed and the oxidation reaction runs inside the zeolite pores.[7] This system is already known to oxidize alcohols, but hitherto nothing is reported about selective oxidations of compounds having both secondary and primary hydroxyl moieties.

Table

entry	starting material	reagent	product[a]	Yield (%)
1	 **1**	H_2O_2/TS-1[b]	 **2**	quant.
2		DMDO[c]		quant.
3	 **3**	H_2O_2/TS-1[b]	 **4**	84
4		DMDO[c]		90
5	 **5**	H_2O_2/TS-1[b]	 **6**	quant.
6		DMDO[c]	 **7**	60
7	 **8**	H_2O_2/TS-1[b]	 **9**	93
8		DMDO[c]	 **10**	60
9	 **11**	H_2O_2/TS-1[b]	no reaction	
10		DMDO[c]	mixture	
11	 **12**	DMDO[c]	 **13**	85
12	 **14**	DMDO[c]	 **15**	82

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[a] All the products are known and the analytical data are in agreement with that reported in literature. [b] As a general procedure, 1 mmol of diol was mixed with 10% of TS-1 and 3 ml of 40% sol. of H_2O_2; acetone was added as cosolvent when necessary, and the mixture was stirred two days. [c] In a tipical procedure the substrate was dissolved in acetone and 1.5 eq. of a 0.07M solution of dimethyldioxirane in acetone were added. The mixture was stirred 18-22 h.

The substrates that we examined have given excellent results. 1,2-pentandiol **1** gave quantitatively the respective 1-Hydroxy-2-pentanone **2**, as well as **3** gave **4** (entries 1, 3). **5** and **8** also gave the selective oxidation of the secondary hydroxyl moiety, although the obtained products were the hemiketals, **6** and **9** respectively (entries 5, 7). The acid catalyzed closure is concerted with the oxidation process and runs while the substrate is still absorbed into the zeolite. In agreement with this mechanism, we treated **7** and **10** with TS-1 in methanol, but no reaction occurred even with longer reaction times. Obviously the fragment CH_3-C=O was not absorbed, and the catalysis by the Lewis acid did not occur. H_2O_2/TS-1 system was already known to be relatively unreactive with cyclic secondary alcohols,[7] **11** in fact did not react in our conditions.

This may be considered the main limit of this method. With the aim to find a good procedure for selective oxidations of cyclic diols too, we considered it interesting to examine the behaviour of DMDO, a relatively new reagent which showed a surprising high efficiency and high selectivity in the oxidation of several functional groups.[8] Moreover acetone is the only organic byproduct of these reactions.

Dioxiranes are already known to oxidize alcohols,[9,10] and a systematic study showed that secondary alcohols are more reactive with methyltrifluoromethyldioxirane[10] than primary ones, in agreement with a different nucleophilicity of the reaction sites.

As reported in the table, the oxidation proceeds quantitatively in the case of close diols such as 1,2 and 1,3 diols (entries 2, 4), while in the cases of 1,4 and 1,5 diols, lower yields of isolated products are obtained (entries 6, 8). That was due to a lower selectivity of the oxidations which lead to a complex mixture of reaction products.

The observed high selectivity is an example of the deactivating effect of the carbonyl group close to the reaction centre. As we noted in previously studies,[11] there is a dipolar interactionn between DMDO and carbonyl groups which can affect the approach of the reagent to the active site. In this case the carbonyl moiety hinders the correct approach of DMDO. The effect is not important when three or more methylene groups are between the hydroxyl moieties. This is the main limit of this method, which, though it works well for close diols, cannot be considered of general value.

Cyclic diols reacted well with DMDO. The 1,2 *cis* diol **12** and the 1,3 diol (mixture of diastereoisomers) gave good yields in the oxidation products **13** and **15**. Otherwise, in the case of **11** the reaction was not selective and we obtained a complex mixture of products The correct approach to the C-H bond of the secondary hydroxy group on **11** is, then, forbidden by the neighbouring CH_2OH moiety, while, for **12**, such interaction does not occur, since the CH_2OH group is in a *trans* configuration with the active site.

The two oxidizing systems that we examined, represent a useful way to selectively oxidize diols with primary/secondary hydroxyl groups. Neverthless, both systems have a very low environmental impact, since they do not produce polluting byproducts and the reactions may even run in wet medium. Generally, we may say that H_2O_2/TS-1 system works well with saturated linear diols, while DMDO is efficient mainly for α and β linear and cyclic diols.

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