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Catalysis by Heteropolyacids: Some New Aspects

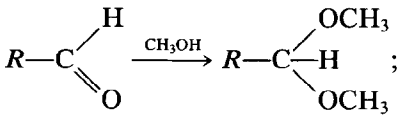
The following types of reactions catalyzed by heteropolyacids are described: (i) acetalization and ketalization of aldehydes and ketones, (ii) transfer hydrogenation of nitro compounds to amino compounds using sodium borohydride as the hydrogen source, and (iii) selective reduction of nitro compounds and ketones in the presence of aldehydes. The latter is an example of bifunctional catalysis involving acetalization and transfer hydrogenation. The results are presented for various substrates in order to demonstrate the generality of the reactions.

INTRODUCTION

Heteropolyacids (HPA) with Keggin structure like phosphomolybdic acid and silicotungstic acid are well-known acid catalysts. Their catalytic activity for a number of acid-catalyzed reactions is very well documented in the literature (*1–5*). The versatility of these catalysts has also been demonstrated by applications in various oxidation reactions (*6–9*). However, there has been very little exploitation of their transfer hydrogenation activity coupled with acid catalysis.

In the present note, we report the following types of reactions catalyzed by HPA:

(i) acetalization/ketalization of aldehydes and ketones:



(ii) transfer hydrogenation of nitro compounds to amino compounds in the presence of $NaBH_4$ as the hydrogen donor;

(iii) selective hydrogenation of nitro compounds and ketones in the presence of aldehydes.

The first reaction is a typical acid-catalyzed reaction. Acetalization or ketalization reactions are the general methods of protecting the aldehyde and keto groups in synthetic organic chemistry. This is achieved by a number of methods using ethanolic HCl, *p*-toluene sulfonic acid, $FeCl_3$, $ZnCl_2$, montmorillonite clays and lanthanides (*10–15*). The HPA-catalyzed process has large turnover numbers and in terms of simplicity, convenience, and elegance this method compares well with the lanthanide-catalyzed acetalization or ketalization (*15*). These aspects will become apparent from the results reported in this note. It should be mentioned, however, that HPA-catalyzed ketalization of cyclohexanone was reported earlier (*16*). In this paper, we have attempted to generalize this observation on a series of aliphatic and aromatic aldehydes and a few ketones.

The second reaction reported in this note refers to a new catalytic aspect of heteropolyacids. We report, for the first time, the transfer hydrogenation activity of phosphomolybdic acid toward nitro compounds to produce amino compounds in the presence of $NaBH_4$ as the source of hydrogen. Similar transfer hydrogenation activity is known with the elements Pd, Ni, and Co (*17*).

The third reaction is essentially an example of bifunctional catalysis by HPA, wherein acid-catalyzed acetalization of aldehyde protects the aldehyde from attack by $NaBH_4$ while HPA catalyzes the transfer hydrogenation of the nitro compound to the amino compound. The selective reduction of ketones in the presence of aldehydes with HPA and $NaBH_4$ is, of course, a result of protecting the latter preferentially while leaving ketone free for borohydride attack. While the selective reduction of ketones in

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the presence of aldehydes is reported with other reagents/catalysts (*14, 15*), selective reduction of nitro compounds in the presence of aldehydes under transfer hydrogenation conditions is not known.

EXPERIMENTAL

Materials. The aldehydes, ketones, and nitro compounds were either procured from Fluka (Switzerland) or Aldrich Chemical Co., Ltd. (UK) and were of 99.5% purity. Molybdophosphoric acid, tungstosilicic acid, sodium borohydride, and the solvents were procured from British Drug House, India.

Reaction procedure for acetalization/ketalization. In a typical reaction using benzaldehyde, 0.02 mol of the aldehyde was mixed with 30 ml of dry methanol in a round-bottomed flask. One-tenth of a gram of HPA[1] ($H_4SiW_{12}O_{40} \cdot XH_2O$ or $H_3PMo_{12}O_{40} \cdot XH_2O$) was added to the flask and the mixture stirred with a magnetic stirrer for 5 to 10 min at room temperature. Then, 0.2 g of $NaBH_4$ was added to trap the water produced in the reaction and drive the reaction to completion. Methanol was evaporated on a rotary evaporator and the reaction mixture was diluted with either diethyl ether or dichloromethane. The ether layer was washed with water and dried on anhydrous sodium sulfate. Ether was evaporated to recover the acetal. The product was identified by IR and NMR and quantification of the reaction products was carried out by GC analysis using PEG 400 on chromosorb as the column.

Reaction procedure for nitro group reduction. Nitro compound (0.005 mol) was placed in a round-bottomed flask along with 25 ml methanol and 0.4 g molybdophosphoric acid. To this, 2 g of $NaBH_4$ was added in small portions and the reaction was carried out at room temperature. After the addition was complete, the reaction mixture was stirred for 30 min. Product was separated from the reaction mixture with dichloromethane or ethyl acetate and purified by column chromatography.

Reaction procedure for selective reduction. In a typical reaction procedure, 0.01 mol each of a ketone and of an aldehyde or 0.005 mol each of a nitro compound and of an aldehyde were placed in 30 ml of methanol in a round-bottomed flask and a weighed quantity of HPA catalyst was added. Then, 2 g of $NaBH_4$ was added slowly and the reaction mixture stirred for 5 to 10 min. The workup procedure after the reaction is as follows. In the case of selective reduction of the nitro compound in the presence of an aldehyde, methanol was evaporated, the products were extracted into dichloromethane and washed with water, and the organic layer was chromatographed on neutral alumina to isolate the amino compound and recover the unreacted acetal. The acetal was hydrolyzed back to the aldehyde. The crude mixture, before isolation of the products, was analyzed by GC. In the case of selective reduction of ketones in the presence of aldehydes, the reaction mixture was treated with 1 *M* HCl to hydrolyze the acetal, extracted with dichloromethane, washed with water, and dried on anhydrous sodium sulfate. This mixture was analyzed by GC.

RESULTS AND DISCUSSION

Table 1 gives the results for acetalization of aldehydes and ketalization of ketones.

It is evident that all the aldehydes studied are acetalized in very high yields. In most of the cases the yields are more than 95%. However, the ketones are not that easily ketalized. While cyclohexanone is ketalized with a yield of 87.8%, the corresponding yields for cyclopentanone and cycloheptanone are 51.1 and 11.8%, respectively. The aromatic ketone, acetophenone, is ketalized only to the extent of 4 to 5%.

One important point to note in our acetal/ketal reactions is that $NaBH_4$, rather than the conventional trimethyl orthoformate, (*15*), is used as a scavenger for water. It

[1] It was found later on that the reactions were equally facile even with 30 mg of HPA.

TABLE 1

HPA-Catalyzed Acetalization and Ketalization

Entry	Substrate	Catalyst (HPA)	Yield of[a] acetal/ketal
1	Benzaldehyde (0.01 mol)	Molyphosphoric acid (0.2 g)	100%
2	Orthonitrobenzaldehyde (0.01 mol)	Tungstosilicic acid (0.4 g)	83%
3	4-Methoxybenzaldehyde (0.02 mol)	Tungstosilicic acid (0.08 g)	95%
4	3,4-Dimethoxybenzaldehyde (0.02 mol)	Tungstosilicic acid (0.08 g)	98%
5	3,7-Dimethyl-2,6-octadienal (0.02 mol)	Tungstosilicic acid (0.08 g)	98%
6	Hexanal (0.02 mol)	Molyphosphoric acid (0.2 g)	97%
7	Benzaldehyde (0.01 mol)	Tungstosilicic acid (0.04 g)	100%
8	Cyclohexanone (0.05 mol)	Tungstosilicic acid (0.16 g)	87.8%
9	Cyclopentanone (0.05 mol)	Tungstosilicic acid (0.16 g)	51.1%
10	Cyclopentanone (0.05 mol)	Tungstosilicic acid (0.16 g)	11.8%

[a] Unconverted starting material constitutes the balance.

appears that $NaBH_4$ generates $NaB(OCH_3)_4$ and/or $NaOCH_3$ *in situ*, which traps water produced in the reaction. The importance of using $NaBH_4$ as the water scavenger becomes apparent in the reactions of selective reductions described in Table 3. $NaBH_4$ acts as a water scavenger for acetal reaction as well as the hydrogen donor for the hydrogenation reaction.

Table 2 assembles data for transfer hydrogenation of nitro compounds to amino compounds. From the table, it appears that the reaction is a general one, giving 100% yields of the amino compounds. Based on spectroscopic evidence (using XPS, ESR, IR, and P^{31} NMR), it is speculated that initially Mo^{6+} is reduced by $NaBH_4$ to a mixture of Mo^{5+} and Mo^{4+}, which is stabilized by the stable Keggin structure (*18*). The Mo^{5+} or Mo^{4+} species are suggested to be responsible for activating the NO_2 group for hydride attack by $NaBH_4$. It was confirmed from spectroscopic evidence that molybdenum was not reduced to oxidation states lower than 4+.

Table 3 lists results for selective reductions of ketones and nitro groups in the presence of aldehydes. Entries 1 to 3 give examples of nitro group reduction in the presence of aldehyde group. In entry 1, nitrobenzene is quantitatively converted to aniline while benzaldehyde is recovered as the acetal to the extent of 95.5%. Aniline and the acetal can, of course, be separated by chromatographing on neutral alumina and the acetal hydrolyzed back to the aldehyde as already mentioned under Experimental. This reaction was extended further to O-nitrobenzaldehyde, which forms O-aminobenzaldehyde dimethylacetal in 100% yield (see Entry 2). Entry 3 is an example wherein nitrobenzene is selectively reduced to aniline to the extent of 90% in the presence of cyclohexanone. While 5% cyclohexanone remains unreacted, the ketal is formed to the extent of 87% and the cyclohexanol formed is only 8%. Entries 4–6 are examples of selective reductions of ketones in the presence of aldehydes, while entries 7 and 8 refer to selective reductions of acetophenone and cycloheptanone, re-

TABLE 2

Molybdophosphoric Acid-Catalyzed Hydrogenation of Nitro Compounds

Entry	Substrate	Results	
1	Nitrobenzene	Aniline	100%
2	2-Nitroanisole	2-Methoxyaniline	100%
3	4-Nitroaniline	1:4 Phenylene diamine	100%
4	4-Nitrodiphenylamine	4-Aminodiphenylamine	100%

TABLE 3

Selective Hydrogenations Using HPA Catalysts[a]

Entry	Substrate 1	Substrate 2	Results	
1	Benzaldehyde (0.005 mol)	Nitrobenzene (0.005 mol)	Aniline	100%
			Benzaldehyde (as acetal)	95.5%
			Benzylalcohol	3.5%
2	Orthonitrobenzaldehyde (0.01 mol)	—	Orthoaminobenzaldehyde acetal	100%
3	Cyclohexanone (0.005 mol)	Nitrobenzene (0.005 mol)	Aniline	90%
			Nitrobenzene	10%
			Cyclohexanone ketal	87%
			Cyclohexanol	8%
			Cyclohexanone	5%
4	Cyclopentanone (0.01 mol)	Hexanal (0.01 mol)	Cyclopentanol	100%
			Hexanal	96.3%
			Hexyl alcohol	3.7%
5	Acetophenone (0.01 mol)	Hexahydrobenzaldehyde (0.01 mol)	Sec. Phen ethyl alcohol	100%
			Hexahydrobenzaldehyde	97.1%
			Cyclohexyl methanol	2.9%
6	Cycloheptanone (0.01 mol)	Hexanal (0.01 mol)	Hexanal	100%
			Cycloheptanol	100%
7	Cyclohexanone (0.01 mol)	Acetophenone (0.01 mol)	Cyclohexanone	86.6%
			Cyclohexanol	13.4%
			Methylphenyl carbinol	100%
8	Cyclohexanone (0.01 mol)	Cycloheptanone (0.01 mol)	Cyclohexanone	82.2%
			Cyclohexanol	17.8%
			Cycloheptanone	3.2%
			Cycloheptanol	96.8%

[a] Catalyst: for the first three entries 0.4 g of molybdophosphoric acid was used; for the rest of the entries 0.08 g of tungstosilicic acid was used.

spectively, in the presence of cyclohexanone. The last two examples take advantage of the fact that cyclohexanone forms the ketal more readily than either acetophenone or cycloheptanone.

Control experiments in the absence of HPA indicated that $NaBH_4$ reduced both the aldehyde and the ketone in the mixture. Further, it was found that $NaBH_4$ could not reduce the nitro group by itself, as is already well known.

We also found that the transfer hydrogenation of the nitro compounds to amino compounds using $NaBH_4$ could be carried out quantitatively using ammonium paramolybdate as the catalyst instead of heteropolyacid. However, in this case a black precipitate of molybdenum metal was observed immediately after the addition of the sodium borohydride. Ammonium paramolybdate, as is to be expected, did not catalyze the acetalization reaction of the aldehydes.

The essential differences between ammonium paramolybdate and HPA are: (i) HPA is capable of bifunctional catalysis, viz., acid-catalyzed acetalization as well as nitro group reduction, while ammonium paramolybdate is capable only of nitro group reduction; it is this characteristic feature of HPA that allows selective reduction of nitro compounds in the presence of aldehydes; (ii) during nitro group reduction, the Keggin structure was found to be retained in the case of HPA; this makes it possible to reuse the catalyst for nitro reduction to achieve quantitative conversion. In the case of ammonium paramolybdate, molyb-

denum metal was found to be precipitated, which is probably the species activating the nitro group. When this catalyst was reused, it gave only about 75% reduction of nitrobenzene to aniline.

In summary, some of the new aspects of HPA catalysis described in this note widen the scope and versatility of the heteropolyacids as catalysts. Currently, work is in progress to explore the use of HPA catalysts for transfer hydrogenations of various other substrates.

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