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Heteropoly Acids, Their Salts and Polyoxometalates as Heterogenous, Efficient and Eco-Friendly Catalysts in Organic Reactions: Some Recent Advances

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In this review article, some recent advances of applying heteropoly acids and polyoxometalates as heterogeneous, reusable and eco-friendly catalysts in organic synthesis are discussed.

Keywords: Heteropoly acids, Polyoxometalates, Heterogenous and Eco-friendly catalyst, Organic synthesis

INTRODUCTION

In recent decade, using an applicable industrial catalyst that is eco-friendly, green and simply recycled in the reaction mixtures has been under attention. Thus, green chemistry has been defined as a set of principles that reduces or eliminates the use or generation of hazardous substances throughout the entire life of chemical materials [1]. If one compares the technology with medical care, Green/Sustainable Chemistry (GSC) focuses on precaution (or prevention) rather than diagnosis and cure [1]. Along this line, using heteropoly acids (HPAs), their salts and polyoxometalates (POMs) which are low in toxicity, highly stable towards humidity, recyclable and air stable have found more attention. These compounds show very high catalytic activity for some acid-catalyzed reactions. HPAs are usually solids that are insoluble in non-polar solvents but highly soluble in polar ones. The use of HPAs in non-polar solvents improves product selectivity and also provides easy separation of HPAs from the reaction mixture [2,3]. Heterogeneous catalysis has become attractive in view of the increasingly strict environmental legislation, in view of their isolation and separation from the reaction media. Solid acid catalysts are harmless to the environment with respect to corrosiveness, safety, quantity of waste, and separability with certainly some exceptions. The catalytic activities of solid acids are usually suppressed significantly in the presence of water. It has been demonstrated that the acidic cesium salts of HPAs are very water-tolerant catalysts for hydration of olefins [4] and hydrolysis of esters [5]. This nature was assigned to moderate hydrophobicity of the catalysts [6].

Heteropoly acids are more active catalysts than conventional inorganic and organic acids for various reactions in solutions [2,3]. A variety of organic reactions that are catalyzed by Brønsted acids such as H_2SO_4, HCl, and other protonic acids or Lewis acids such as $AlCl_3$, $FeCl_3$, etc. proceeded in the presence of solid Heteropoly acids or polyoxometalates, more efficiently, under milder conditions, with greater selectivity, better yields, shorter reaction times and etc.

In the following sections some recent transformations which are conducted in the presence of heteropoly acids (HPAs), their salts, and also polyoxometalates are discussed.

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HETERO-MICHAEL ADDITION

Hetero-Michael addition reaction, especially the conjugate addition of thiols to α,β-unsaturated carbonyl groups constitutes a key reaction for the preparation of organsulfur compounds. Organosulfur compounds have become increasingly useful and important in the synthesis of biologically active compounds such as the calcium antagonist diltiazem as well as in organic synthesis [7,8]. There are some reports available for the addition of thiols to α,β-unsaturated carbonyl compounds catalyzed by Lewis acids [9,10].

The choice of $H_3PW_{12}O_{40}$ as an 'eco-friendly' promoter represents a further advance in practicability and atom economy in these reactions. In fact, in the presence of 1 mol% of the $H_3PW_{12}O_{40}$, hetero-Michael addition reaction works well in CH_3CN at room temperature [11]. In addition, the work-up procedure allows the complete recovery of the catalyst, which can be reused without an appreciable loss of its activity. Some selected data are reported in Table 1. They show that the protocol is general and efficient for a variety of substrates.

The double Michael addition of dithiols to α,β-unsaturated cyclic and acyclic ketones has been performed smoothly in the presence of $H_3PW_{12}O_{40}$ (1 mol %) in high yields. These compounds are potential precursors for the preparation of macrocyclic or polymeric compounds carrying sulfur heteroatoms. Some of the representative reactions are shown in Table 2.

FRIEDEL-CRAFTS REACTIONS

Friedel-Crafts acylation of aromatic compounds is the most important and practical route for the synthesis of aromatic ketones that are used in manufacturing of fine chemicals as well as pharmaceuticals [12]. The acylating agents for the synthesis of aromatic ketones by Friedel-Crafts reactions are mostly acid anhydrides or acyl chlorides. For this purpose, varieties of catalysts have been reported [13,14].The use of carboxylic acids, as acylating agents, are scarcely reported [15] which is a superior method with respect to the procedures utilizing acyl chlorides and anhydrides for the preparation of aryl ketones. Carboxylic acids are stable and more available compounds and their handlings are much easier than their corresponding acyl chlorides and anhydrides.

Benzoylation and Acylation of Aromatic Compounds

Aluminumdodecatangstophosphate ($AlPW_{12}O_{40}$) under solvent-less conditions catalyzes efficiently acylation and benzoylation of aromatic compounds under mild conditions (Table 1) [16a]. The advantage of this method is the use of catalytic amounts of $AlPW_{12}O_{40}$ (3-4 mol%) and its ease of handling in comparison with $AlCl_3$ which should be used in more than a molar ratio and it is a highly corrosive and toxic compound with high moisture sensitivity.

Direct Carbonylation of Aromatic Compounds with Carboxylic Acids in the Presence of Trifluoroacetic Anhydride

$AlPW_{12}O_{40}$ also catalyzes direct Friedel-Crafts carbonylation of aromatic compounds in the presence of trifluoroacetic anhydride in solvent-free conditions at room temperature [16b]. The results of this study are presented in Table 4.

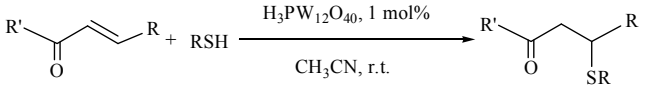
Direct Acylation of Anisole with Carboxylic Acids

Direct carbonylation of anisole has been conducted in the presence of catalytic amount of $AlPW_{12}O_{40}$ (6 mol%) at 120 ºC under neat conditions [16a]. The reaction proceeded well with structurally diverse carboxylic acids. Some of the results are presented in Table 5.

TRIMETHYLCYANOSYLILATION OF CARBONYL GROUPS

Cyanohydrins are highly versatile synthetic intermediates, which can easily be converted into a wide variety of important synthetic intermediates including α-substituted acids, ketones, aldehydes and α-hydroxy amines. One of the most straightforward entries to this important goal is through their cyanohydrin preparation [17]. They are also components of commercially important compounds such as the pyrethroid insecticides, cypermetrin and fluvaliate [18]. Preparation of cyanohydrins by the addition of highly toxic HCN to carbonyl group is not a straightforward process and needs serious precaution. The other problem which affects the yields of the products stems from the existence of inevitable equilibrium

Table 1. Conjugative Addition of Thiols to α,β-Unsaturated Cyclic and Acyclic Ketones in CH_3CN Catalyzed by $H_3PW_{12}O_{40}$ (1 mol%) at Room Temperature



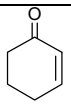
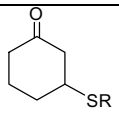
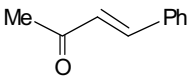
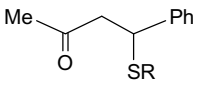
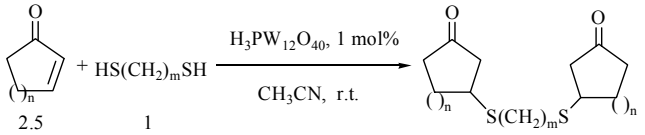
Entry	α,β-Unsaturated Carbonyl Compound	Product	Time (min)	Yield [a] (%)
				
1	″	R = Ph	5	95
2	″	R = *p*-MePh	5	92
3	″	R = phCh$_2$	5	98
4	″	R = Cyclohexyl	10	90
				
13	″	R = Ph	45	98
14	″	R = *p*-MePh	45	96
15	″	R = PhCH$_2$	60	93

Table 2. Double Conjugative Addition of Dithiols to α,β-Unsaturated Cyclic and Acyclic Ketones in CH_3CN Catalyzed by $H_3PW_{12}O_{40}$ (1 mol %) at Room Temperature



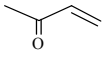
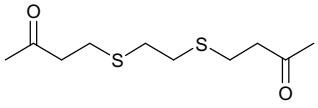
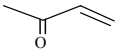
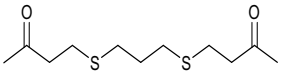
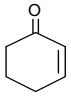
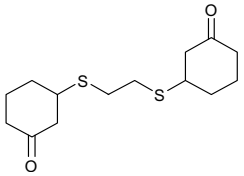
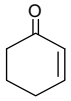
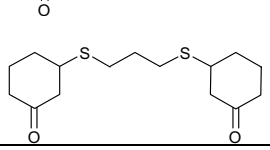
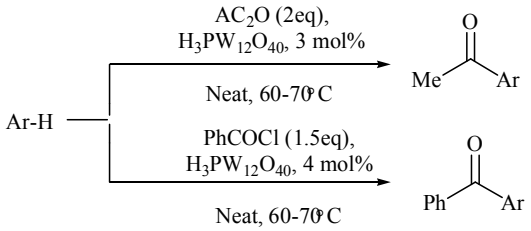
Entry	α,β-Unsaturated Carbonyl Compound	Product	Time (min)	Yield [a] (%)
1			15	85
2			15	81
3			30	75
4			30	73

Table 3. Acylation of Aromatic Compounds with Acetic Anhydride Catalyzed by $AlPW_{12}O_{40}$



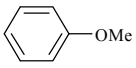
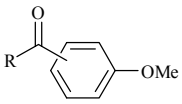
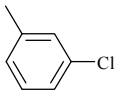
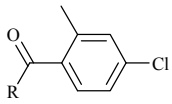
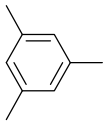
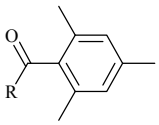
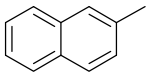
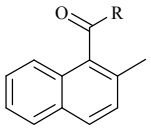
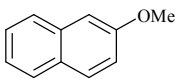
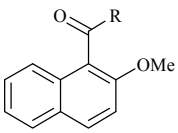
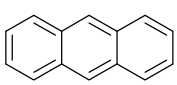
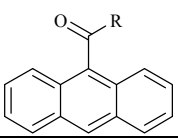
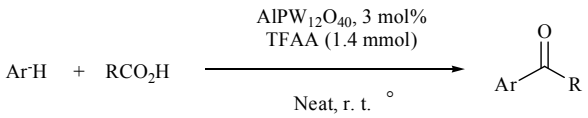
Entry	Ar-H	Acetic anhydride, or Benzylyc chloride	Product		Time (h)	Yield (%)
1		Acetic anhydride (*O*: *P* = 12:88)		R = Me	0.75	94
2		Benzoyl chloride (*O*: *P* =1:4)		R = Ph	2	94
3		Acetic anhydride		R = Me	6	91
4		Benzoyl chloride		R = Ph	4.5	91
5		Acetic anhydride		R = Me	2.5	92
6		Benzoyl chloride		R = Ph	3	92
7		Acetic anhydride		R = Me	5.5	90
8		Benzoyl chloride		R = Ph	2.5	91
9		Acetic anhydride		R = Me	4	85
10		Benzoyl chloride		R = Ph	1.7	94
11		Acetic anhydride		R = Me	2.6	90
12		Benzoyl chloride		R = Ph	4	88

Table 4. $AlPW_{12}O_{40}$ Catalyzed Carbonylation of Aromatic Compounds with Carboxylic Acids in the Presence of Trifluoroacetic Anhydride



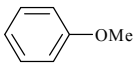
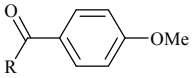
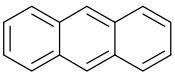
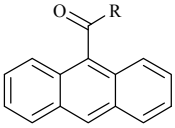
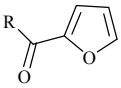
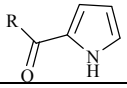
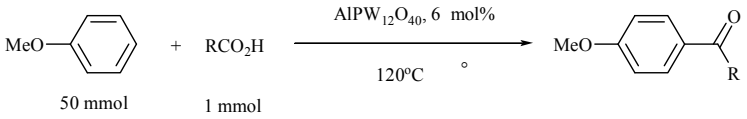
Entry	Ar-H	RCO_2H	Product	Time (h)	Yield (%)
1		CH_3CO_2H	 $R = CH_3$	0.25	94
2		$C_7H_{15}CO_2H$	$R = C_7H_{15}$	1.5	91
3		$PhCH_2CO_2H$	$R = PhCH_2$	2	94
4		$PhCO_2H$	$R = Ph$	2.5	96
5		CH_3CO_2H	 $R = CH_3$	2.5	78
6		$PhCH_2CO_2H$	$R = PhCH_2$	10	71
7		$PhCO_2H$	$R = ph$	8.5	69
8		CH_3CO_2H	 $R = CH_3$	1.25	94
9		$PhCH_2CO_2H$	$R = PhCH_2$	1.5	95
10		$PhCO_2H$	$R = Ph$	2.5	98
11		CH_3CO_2H	 $R = CH_3$	2.5	92
12		$PhCO_2H$	$R = Ph$	0.4	98

Table 5. Carbonylation of Anisole with Carboxylic Acids Catalyzed by Reusable $AlPW_{12}O_{40}$ at 120 °C [a]



Entry	Carboxylic acid	Time (h)	Yield (%)
1	Acetic acid	3	85
2	Propionic acid	3.5	88
3	Butyric acid	5	87
4	Hexanoic acid	1.5	91
5	Octanoic acid	4	85
6	Dodecanoic acid	8	90
7	Benzoic acid	10	92

condition between the reactants and the adduct product. In order to surmount this problem, the reaction of TMSCN with carbonyl groups in the presence of Lewis acid or Lewis base catalysts has been under attention in the last decade [19]. However, general, mild, and high-yielding protocols for cyanation of hindered carbonyl groups are still very limited in the literature.

$H_3PW_{12}O_{40}$ has been applied successfully for the high yielding cyanation of carbonyl compounds with TMSCN in the absence of solvent as shown in Table 6 [20]. This catalyst has been also very effective for the cyanation of sterically hindered ketones such as shown in Scheme 1.

PREPARATION OF SYMMETRICAL AND UNSYMMETRICAL ETHERS

Preparation of ethers is an important reaction for which a wide variety of procedures have been developed during the last decades. The most commonly used protocol is Williamson ether synthesis [21] which requires initial transformation of alcohols into their corresponding halides or tosylates followed by their displacement with strongly basic alkoxides or phenoxides. Strong basic condition is hazardous to complex molecules carrying base sensitive functional groups. Etherification by direct condensation of alcohols has been considered as an alternative which is conducted in the presence of catalytic amounts of organic or inorganic protic acids [22]. Lewis acids have been also used for direct etherification condensation reactions [23,24]. In most cases, the reactions suffer from the use of stoichiometric amounts of the Lewis acids which is due to their decomposition by water generated in the process of etherification reactions [23].

Reductive etherification of carbonyl compounds by $BiBr_3/Et_3Si$-H and $BiBr_3/ClR_2Si$-H are also reported [25]. However, these systems suffer from being highly water sensitive, expensive and not easily available.

Catalytic amount (5 mol%) of aluminumdodeca-tangsto-phosphate ($AlPW_{12}O_{40}$) has been used for etherification of primary, secondary and tertiary benzylic alcohols with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol and *t*-butanol to produce benzyl alkyl ethers in short reaction times in excellent yields (Table 7) [26]. Symmetrical dibenzyl ethers from their corresponding alcohols have been also prepared in the presence of 7 mol% of $AlPW_{12}O_{40}$ at room temperature in CH_2Cl_2 [26]. The results of this study are summarized in Table 8.

CHEMOSELECTIVE PROTECTION OF THIOLS

Protection of one functional group in the presence of the other groups is an essential task for the synthesis of complex molecules. The protection of SH functional group is rather rare in the literature and is important because of the reactivity of this functionality as a nucleophile and also its sensitivity to oxidation both by dimerisation and *S*-oxide formation [27].

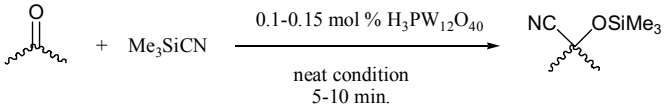
Selective protection of SH versus OH groups by diphenyl methanol (DPM) in the presence of catalytic amount of $AlPW_{12}O_{40}$ (7 mol%) has been successfully performed in high yields [27b]. By this method, various aliphatic and aromatic thiols and acid-sensitive substrates like furfurylmercaptan were converted efficiently into diphenylmethyl thioethers in high yields at room temperature in CH_2Cl_2 [28]. The results of this study are presented in Table 9.

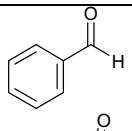
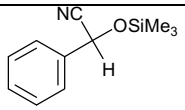
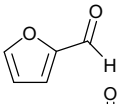
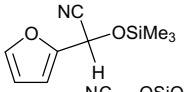
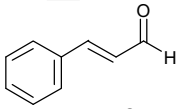
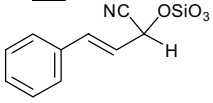
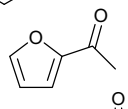
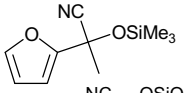
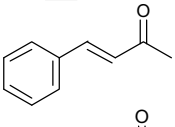
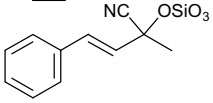
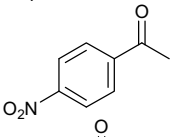
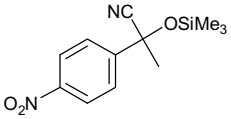
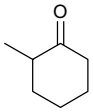
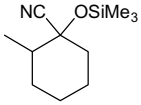
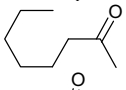
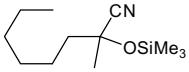
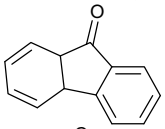
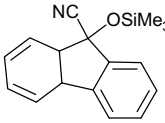
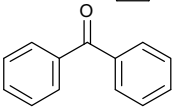
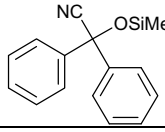
This catalyst effects protection of thiols very selectively and efficiently in the presence of hydroxyl groups [28]. Thus, 2-thioethanol (1.1 mmol) and diphenylmethanol (1 mmol) in the presence of $AlPW_{12}O_{40}$ (4 mol%) has produced 2-benzhydrylsulfanyl ethanol in 95% yield at room temperature in which OH functional group remains intact (Scheme 2). This selectivity has been also demonstrated in competition experiments as shown in Scheme 3.

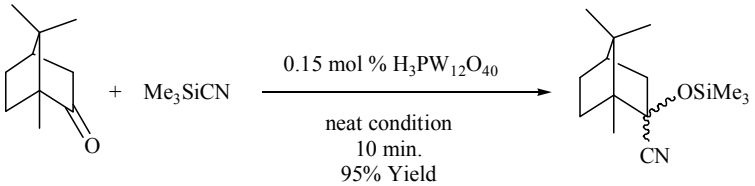
THIOACETALIZATION AND TRANSTHIOACETALIZATION OF CARBONYL GROUPS

The protection of carbonyl groups as acetals or thioacetals is often necessary during the synthesis of multi-functional complex molecules [27b] and natural products [29]. Generally, thioacetals have been prepared by the condensation of carbonyl compounds and thiols catalyzed with protic acids [30], solid acids [31], (such as H-Y or H-mordenite Zeolite, Nafion-H, Amberlyst-15), Lewis acids [32,33] or solid supports [34]. Transthioacetalization of acetals has also been conducted in the presence of $CoCl_2$-Me_3SiCl [35a], and natural kaolinitic clay [35b].

Table 6. $H_3PW_{12}O_{40}$ (0.1-0.15 mol%) Mediated TMSCN Addition to Carbonyl Groups under Neat Conditions at Room Temperature

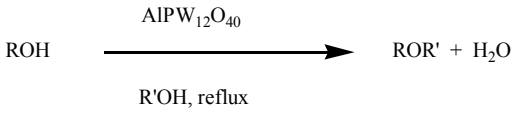


Entry	Substrate	Product	Yield
1			92
2			90
3			94
4			93
5			97
6			98
7			94
8			96
9			97
10			98



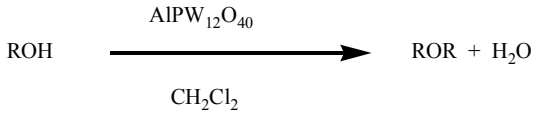
Scheme 1

Table 7. Etherification of Benzylic Alcohols with Different Alcohols in the Presence of 5 mol% of $AlPW_{12}O_{40}$ under Reflux Conditions



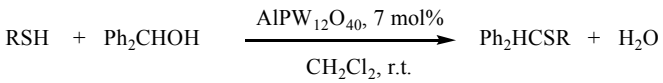
Entry	Alcohol	Solvent	Time (h)	Yield (%)
1	*p*-$MeOC_6H_4CH_2OH$	Methanol	0.15	91
2	″	Ethanol	0.15	93
3	″	1-Propanol	0.15	93
4	″	2-Propanol	0.15	90
5	″	*t*-Butanol	0.25	92
6	$PhCH(OH)CH_3$	Methanol	7	83
7	″	Ethanol	7	86
8	″	1-Propanol	0.5	95
9	″	1-Butanol	0.1	93
10	″	2-Butanol	0.15	90
11	*p*-$MeC_6H_4CH_2OH$	1-Propanol	1	93
12	″	1-Butanol	0.75	95
13	″	2-Butanol	1.3	89

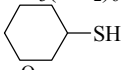
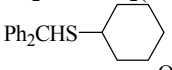
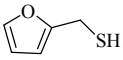
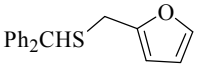
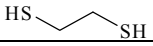
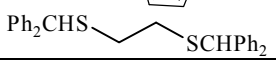
Table 8. Preparation of Symmetrical and Unsymmetrical Ethers in the Presence of 7% mol of $AlPW_{12}O_{40}$ as a Heterogeneous Catalyst

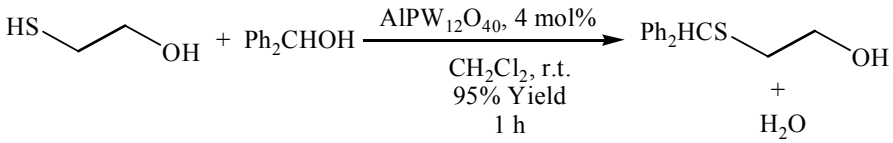


Entry	Alcohol	Product	Time (h)	Yield (%)
1	$PhCHOHCH_3$	$(PhCHCH_3)_2O$	3	94
2	Ph_2CHOH	$(Ph_2CH)_2O$	1	92
3	*p*-$MeOC_6H_4CH_2OH$	(*p*-$MeOC_6H_4CH_2)_2O$	0.33	87
4	$PhCH_2OH$	$(PhCH_2)_2O$	1	86
5	*p*-$MeC_6H_4CH_2OH$	(*p*-$MeC_6H_4CH_2)_2O$	0.7	91
6	*p*-$ClC_6H_4CH_2OH$	(*p*-$ClC_6H_4CH_2)_2O$	1.2	96
7	*p*-$NO_2C_6H_4CH_2OH$	(*p*-$NO_2C_6H_4CH_2)_2O$	10	98
8	*p*-$PhC_6H_4C(Me)_2OH$	*p*-$PhC_6H_4C(Me)_2)_2O$ (60%) + *p*-$PhC_6H_4(Me)C{=}CH_2$ (40%)	3.5	93

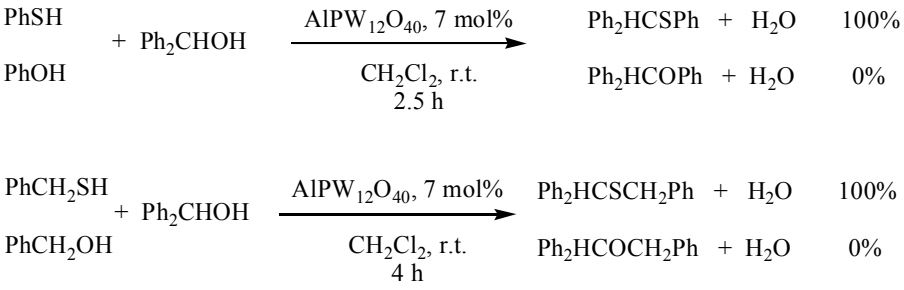
Table 9. Protection of Thiols with DPM in the Presence of a Catalytic Amount of $AlPW_{12}O_{40}$ (7 mol%) in CH_2Cl_2 at Room Temperature



Entry	Substrate	Product	Time (h)	Isolated yield (%)
1	PhSH	Ph_2CHSPh	2	92
2	*p*- MeC_6H_4SH	$Ph_2CHSC_6H_4$-*p* -Me	4	96
3	$PhCH_2SH$	Ph_2CHSCH_2Ph	4	90
4	$CH_3CH_2CH_2SH$	$Ph_2CHSCH_2CH_2CH_3$	24	81
5	$CH_3(CH_2)_6CH_2SH$	$Ph_2CHSCH_2(CH_2)_6CH_3$	16	86
6			5.5	95
7			9	92
8			6	92

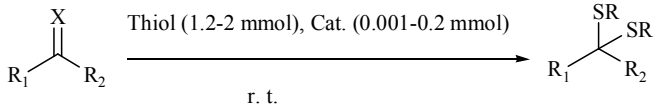


Scheme 2



Scheme 3

Table 10. Thioacetalization of Carbonyl Compounds, Acetals, Ketals, O, S-acetals and Acylals Catalyzed by Tungstophosphoric Acid ($H_3PW_{12}O_{40}$)

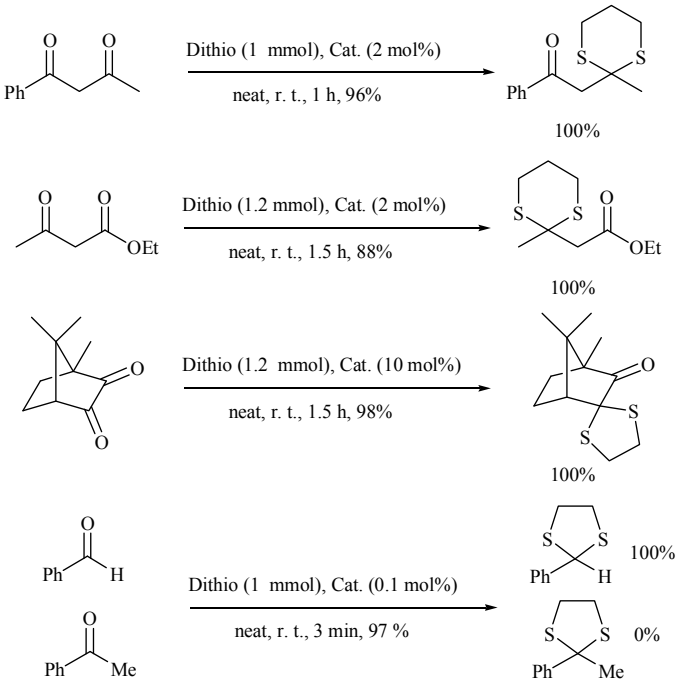


Entry	R_1	R_2	X	R	Sub./Thiols/Cat.	Time (min)	Yield (%)
1	Ph	H	O	$(CH_2)_3$	1: 1.2: 0.001	2.5	98
2	Ph	H	O	Ph	1: 1.2: 0.01	10	97
3	Ph	H	O	n-Bu	1: 1.2: 0.01	25	97
7	n-C_5H_{11}	H	O	$(CH_2)_3$	1: 1.2: 0.001	3	89
8	PhCH=CH	H	O	$(CH_2)_3$	1: 1.2: 0.001	2	91
9	$PhCH_2$	CH_3	O	$(CH_2)_3$	1: 1.5: 0.001	10	96
10	-$(CH_2)_5$-		O	$(CH_2)_3$	1: 1.2: 0.001	4	98
11	Ph	CH_3	O	$(CH_2)_2$	1: 1.5: 0. 02	70	98
13	(+)-camphor		O	$(CH_2)_3$	1: 2 : 0.2	24 (h)	89
14	Ph	H	$(OMe)_2$	$(CH_2)_3$	1: 1.2: 0. 004	5	98
17	p-MeC_6H_4	H	-$O(CH_2)_3S$-	$(CH_2)_3$	1: 1.2: 0. 01	8	96
19	Ph	CH_3	-$O(CH_2)_3O$-	$(CH_2)_3$	1: 1.2: 0. 02	2 (h)	94
20	p-MeC_6H_4	H	$(OAc)_2$	$(CH_2)_3$	1: 1.2: 0. 01	4	98

$H_3PW_{12}O_{40}$ has been applied as a catalyst for the protection of carbonyl compounds by thiols [36]. Various types of aromatic and aliphatic aldehydes have been cleanly and rapidly converted to their corresponding dithioacetals in excellent yields in the presence of a 1.2 molar excess of thiol or dithiol in the presence of a catalytic amount of $H_3PW_{12}O_{40}$ (0.1 mol%) at room temperature (Table 10). $H_3PW_{12}O_{40}$ with respect to the other catalysts such as $(NH_4)_2HPW_{12}O_{40}$, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, TfOH, CH_3SO_3H and H_2SO_4 used for this purpose, shows a superior catalytic activity. The chemoselectivity of the method for the protection of different carbonyl groups using $H_3PW_{12}O_{40}$ are given in Scheme 4.

CHEMOSELECTIVE SILYLATION OF -OH GROUPS BY ACTIVATION OF HEXA-METHYLDISILAZANE (HMDS)

Protection of hydroxyl functional groups is an important process in multi-step synthesis [27b]. One of the popular methods for this purpose is to transfer hydroxyl groups into their corresponding silyl ethers. Hexamethyldisilazane (HMDS) which is a cheap and a commercially available compound can be used for the preparation of trimethylsilyl ethers from hydroxyl compounds. Even though, the handling of this reagent is easy, its main drawback is its poor silylating power which needs forceful conditions and long reaction times [37]. For the activation of HMDS, varieties of catalysts have been reported [38]. $H_3PW_{12}O_{40}$ as a reusable and heterogeneous catalyst has been also applied for efficient and selective O-trimethylsilylation of a wide variety of alcohols and phenols using easily available hexamethyldisilazane (HMDS) at 55-60 °C under solvent-free conditions [39]. The results are shown in Table 11.



Scheme 4

$H_3PW_{12}O_{40}$ is a highly selective catalyst for this purpose and some representative reactions are shown in Scheme 5. A mechanistic pathway has been also provided for the reaction which is shown by Scheme 6.

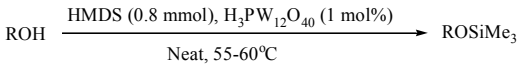
Deprotection of silylethers is also reported by using a catalytic amount of potassium dodecatungestocobaltate trihydrate ($K_5CoW_{12}O_{40}.3H_2O$, 1 mol%) at room temperature in excellent yields (Table 12) [40].

PROTECTION OF -OH, -SH AND -NH_2 BY ACYL GROUP

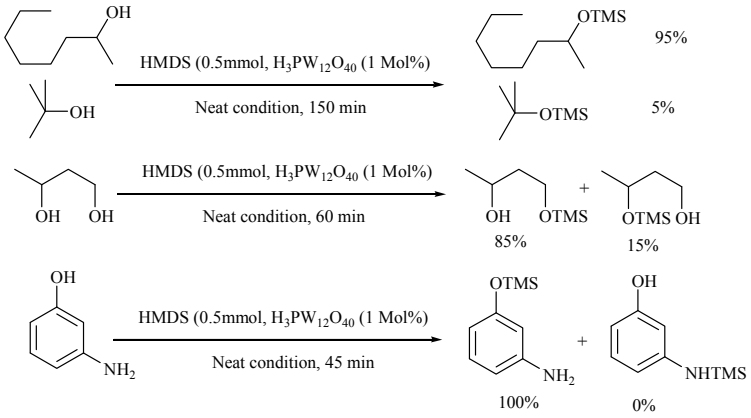
Protection of alcohols, amines, and thiols by acetyl chloride or acetic anhydride is an important transformation reaction in organic synthesis [27b]. For this purpose, acetic anhydride or acetyl chloride in the presence of stoichiometric amounts of amine bases, such as tertiary amines, 4-(dimethylamino) pyridine (DMAP) and tributylphosphine have been used [41]. Protic or Lewis acids have also been used to catalyze acetylation of alcohols [42].

It is reported that a catalytic amount of $AlPW_{12}O_{40}$ (0.1 mol%) would be sufficient for the acetylation of alcohols, thiols and amines in the presence of acetic anhydride at room temperature [43]. Acetylation of benzylic, primary, secondary, hindered tertiary alcohols and phenols are proceeded efficiently in high isolated yields using 1.5 mmol of acetic anhydride and this catalyst. Sensitive alcohols towards acidic conditions were also acetylated under similar reaction conditions in high yields in a short reaction time without giving any by-products. It is also reported that acetylation of amines and thiols to their corresponding acetamides and

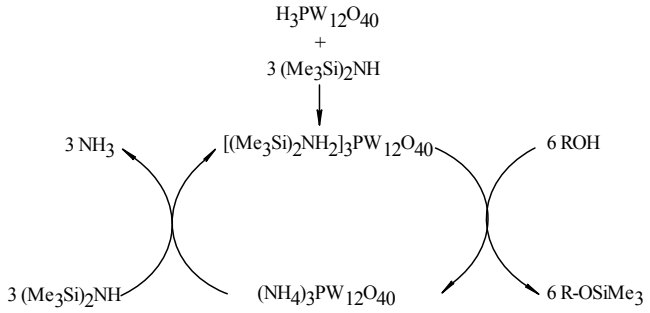
Table 11. Silylation of Alcohols and Phenols Using HMDS in the Presence of $H_3PW_{12}O_{40}$ at 55-60 °C under Solvent-free Conditions



Entry	ROH	Time (min)	Yield (%)
1	$PhCH_2OH$	23	90
2	$4\text{-}ClC_6H_4CH_2OH$	7	82
3	$4\text{-}MeC_6H_4CH_2OH$	6	95
4	$4\text{-}MeOC_6H_4CH_2OH$	20	96
5	$PhCH(OH)CH_3$	16	93
6	$PhCH(OH)CH_2CH_3$	15	95
7	PhCH(OH)Ph	48	93
8	$PhCH_2CH_2CH_2OH$	18	92
9	1-Octanol	7	96
10	2-Octanol	9	93

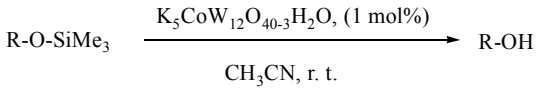


Scheme 5



Scheme 6

Table 12. Deprotection of Silylethers Catalyzed by $K_5CoW_{12}O_{40}.3H_2O$



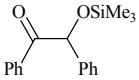
Entry	ROH	Time (min)	Yield (%)
1	$PhCH_2OSiMe_3$	25	100
2	$4\text{-}NO_2C_6H_4CH_2OSiMe_3$	15	100
3	$4\text{-}PhC_6H_4CH(OSiMe_3)Me$	40	96
4	$4\text{-}MeOC_6H_4CH_2OSiMe_3$	25	100
5	$PhCH(OH)CH_3$	16	93
6	$PhCH(OH)CH_2CH_3$	15	95
7	$PhCH(OSiMe_3)Ph$	45	96
8	$PhCH{=}CHCH_2OSiMe_3$	20	100
9		30	100

Table 13. Acetylation of Alcohols, Amines and Thiols Using Ac_2O in the Presence of $AlPW_{12}O_{40}$ as a Catalyst

Entry	Substrate	Time (min)	Yield (%)
1	$4\text{-}OMeC_6H_4CH_2OH$	1	93
2	PhCH(OH)Ph	8	88
3	1,4-Butandiol	5	91
4	Norborneol	12	96
5	(2)-Menthol	11	95
6	Benzoin	95	89
7	Cholesterol	22	87
8	Adamantanol	100	92
9	Terpineol	140	92
10	$(Ph)_2C(OH)CH_3$	200	91
11	$4\text{-}NO_2C_6H_4OH$	12	88
12	2-Naphthol	15	92
13	3-Methyl-2-buten-1-ol	12	91
14	1-Octen-3-ol	5	93
15	3-Hexyne-2,5-diol	15	92
16	Hydroquinone	12	88
17	L-(+)-Ascorbic acid	120	93
18	$4\text{-}NO_2\text{-}C_6H_4NH_2$	12	89
19	PhNH(Me)	10	91
20	$NH(CH_2Ph)_2$	10	96
21	PhSH	2	91
22	$PhCH_2SH$	3	89

thioacetates proceeded well in short reaction times in excellent yields. The results of this study are shown in Table 13. Selectivity of the method is excellent, as is presented by Scheme7.

Hydroxyl group has been also protected by acetic anhydride (Table 14) [44a], acetic acid, ethyl acetate and ethyl formate (Table 15) [44b] catalyzed by potassium dodeca-tungestocobaltate trihydrate ($K_5CoW_{12}O_{40}.3H_2O$). By this recyclable catalyst acetylation and formylation of alcohols and phenols were performed well with excellent yields. The results are shown in Tables 14, 15.

PROTECTION OF ALDEHYDES AS THEIR ACYLALS

Acylals (*geminal* diacetates) or *gem*-bis (acyloxy)-alkanes have been used as protecting groups for carbonyl compounds because of their stability in neutral and basic media [27b] as well as towards aqueous acids [45]. Due to the remarkable stability of *gem* diacetates towards a variety of reactions, they play an important role in organic synthesis for the protection of aldehydes. In the last decade, various catalysts have been reported for this purpose [46]. Reactions of acylals are also important for the preparation of other compounds and have been under investigation recently [47]. Solvent-free reactions have attracted considerable attention in chemical processes due to their safety, economy, easy work up, high yields and usually fast reaction rates [38a, b]. Aluminumdodeca-tugstophosphate ($AlPW_{12}O_{40}$) has been also successfully used for the preparation of acylals from structurally different aldehydes at room temperature under solvent-free conditions (Table 16) [48].

The selectivity of the method is shown by competitive reactions for the acylation of aldehydes in the presence of ketones using $AlPW_{12}O_{40}$ as the catalyst under solvent-free conditions at room temperature (Scheme 8).

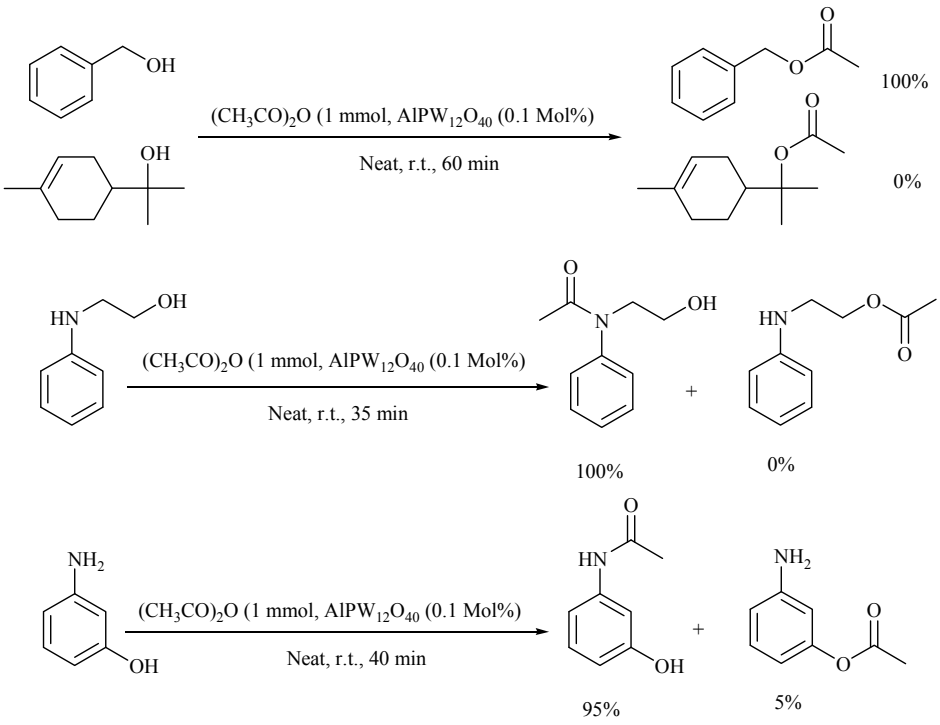
OXIDATION OF AROMATIC AMINES TO THEIR NITRO COMPOUNDS

Oxidation of anilines to their nitro compounds is an important chemical transformation. Oxidation of aromatic primary amines has attracted attention of chemists in recent years [49,50]. The nature of the oxidation products formed depends on the type of the oxidant used and the reaction conditions, *i.e.* aqueous or non-aqueous media and the pH employed for the reaction. For this purpose methods are well documented. Various reagents, including metal compounds, organic peroxides, hydrogen peroxide, have been used to form oxygen-containing derivatives of anilines [51]. Some of the procedures described in the literature suffer from harsh reaction conditions, over-oxidation, low yields of the desired products, and unavailability of the reagents. Non-toxic, low price and an easy available sodium perborate (SPB) ($NaBO_3.nH_2O$, n = 1-4) is extensively used in detergent industry as bleaching, antiseptic agents and in organic synthesis. SPB is a strong substitute and a competitor for the dangerous concentrated H_2O_2. This compound has been extensively used for the functional group oxidation in organic synthesis and is recently reviewed [52]. Sodium perborate ($NaBO_3$) in the presence of catalytic amount of tungstophosphoric acid ($H_3PW_{12}O_{40}$) converts anilines into nitro compounds in micellar media of cetyltrimethyl-ammonium bromide (CTAB) in the absence of organic co-solvents [53].

The effect of several surfactants; cetyltrimethylammonium bromide, CTAB (cationic), sodium dodecylsulfate, SDS (anionic), and TritonX-100 (neutral) at their critical micelle concentration (CMC) in the presence of SPB in water upon the rate of oxidation of aniline has been studied. The results show that CTAB at 10 CMC shows the best micellar activity and enhances chemoselectivity (only nitro compound has been formed) of the reaction. The results are presented in Table 17.

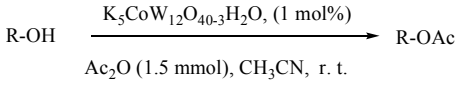
DEPROTECTION OF OXIMES TO CARBO-NYL GROUPS

Oximes are extensively used as preferred derivatives for protection, purification, and characterization of carbonyl compounds [54]. They play an important role as synthetic intermediates en route to nitriles [55], nitro compounds [56], nitrones [57], amines [58], and isoxazolines [59], and also as α-activating group in synthetic organic chemistry [60]. Oxidative deoximation methods which have been developed in recent years [61] consist of toxic metals such as Ce(IV), Pb (IV) and Cr(VI). Regeneration of carbonyl compounds from



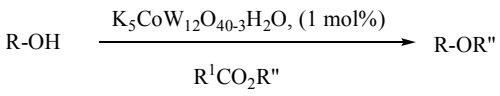
Scheme 7

Table 14. Acetylation of Alcohols and Phenols with Ac_2O Catalyzed by $K_5CoW_{12}O_{40}.3H_2O$ in CH_3CN



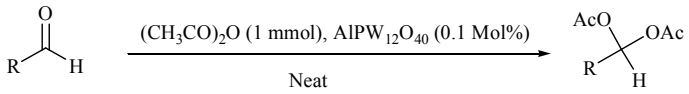
Entry	ROH	Time (min)	Yield (%)
1	$PhCH_2OH$	5	98
2	$4\text{-}MOC_6H_4CH_2OH$	240	87
3	$3\text{-}NO_2C_6H_4CH_2OH$	15	98
4	(-)-Menthol	75	94
5	Ph_3COH	240	90
6	$4\text{-}NO_2C_6H_4OH$	20	100
7	Hydroquinone	15	98
8	1-Naphthol	20	96

Table 15. Esterification of Alcohols Catalyzed by $K_5CoW_{12}O_{40}.3H_2O$ in Reflux Condition

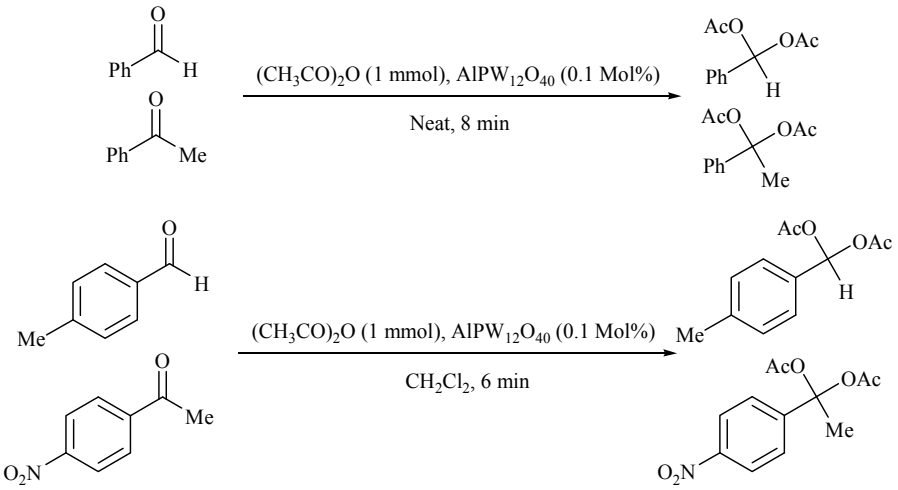


Entry	ROH	R'CO$_2$R"	Time (h)	Yield (%)
1	3-MOC$_6$H$_4$CH$_2$OH	CH$_3$CO$_2$H	0.75	97
2	3-MOC$_6$H$_4$CH$_2$OH	CH$_3$CO$_2$Et	3.5	89
3	3-MOC$_6$H$_4$CH$_2$OH	HCO$_2$Et	1.25	97
4	3-NO$_2$C$_6$H$_4$CH$_2$OH	CH$_3$CO$_2$H	0.75	96
5	3-NO$_2$C$_6$H$_4$CH$_2$OH	CH$_3$CO$_2$Et	5	87
6	3-NO$_2$C$_6$H$_4$CH$_2$OH	HCO$_2$Et	0.75	94
7	(-)-Menthol	CH$_3$CO$_2$H	1	82
8	(-)-Menthol	CH$_3$CO$_2$Et	8	35
9	(-)-Menthol	HCO$_2$Et	1	81
10	Ph$_3$COH	CH$_3$CO$_2$H	2	85
11	Ph$_3$COH	CH$_3$CO$_2$Et	5	80
12	Ph$_3$COH	HCO$_2$Et	1.25	80

Table 16. $AlW_{12}O_{40}$-Catalyzed Formation of *gem*-Diacetates from Aldehydes

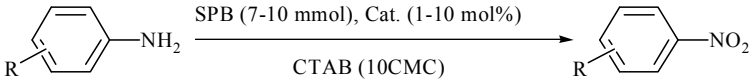


Entry	Substrates	Time (min)	Yield (%)
1	Benzaldehyde	2	89
2	4-Me-Benzaldehyde	1	96
3	4-Cl-Benzaldehyde	6	95
4	2-Cl-Benzaldehyde	5	91
5	3-MeO-benzaldehyde	4	93
6	Anisaldehyde	6	90
7	3-NO2-Benzaldehyde	3	88
8	4-NO2-Benzaldehyde	45	89
9	4-CN-Benzaldehyde	20	88
10	2,6-Dichlorobenzaldehyde	15	95
11	Heptanal	12	92
12	Cinnamaldehyde	5	92



Scheme 8

Table 17. Oxidation of Anilines in the Presence of CTAB and $H_3PW_{12}O_{40}$ by $NaBO_3.4H_2O$ at 55-60 ^oC



Entry	Ar	Yield (%)
1	C_6H_5	91
2	2-$CH_3C_6H_4$	89
3	3-$CH_3C_6H_4$	77
4	4-$CH_3C_6H_4$	88
5	2-$CH_3OC_6H_4$	81
6	4-$CH_3OC_6H_4$	85
7	3,4-$(CH_3O)C_6H_3$	68
8	2-ClC_6H_4	45
9	4-ClC_6H_4	53
10	2-BrC_6H_4	48
11	4-BrC_6H_4	58

oximes by different methods has been extensively reviewed [62]. Some of the reagents are expensive and in some cases, high temperatures are required which lead to by-products. Development of the new procedures in order to eliminate the problems encountered by the existing methods is still of interest to organic chemists. Various metal nitrates have been used for this purpose in different reaction conditions. They consist of copper(II) nitrate supported on silica gel [63], clay supported ammonium nitrate(Clayan) in solvent or under microwave irradiation [64]. $Bi(NO_3)_3$ [65a], $Zn(NO_3)_2$ [65b], $Th(NO_3)_3$ [65c], and $NH_4Ce(NO_3)_4$ (CAN) [65d]. Some other reported procedures suffer from using corrosive mineral acids such as HNO_3 or H_2SO_4, some of them from long reaction times and the other from being unreactive towards aldoximes [59,65].

Catalytic application of $H_3PW_{12}O_{40}$ for the oxidative deprotection of various types of oximes to their corresponding carbonyl compounds using $Fe(NO_3)_3.9H_2O$ and $Bi(NO_3)_3.5H_2O$ as oxidants in the absence of solvent has been reported [66]. The results of the report are summarized in Table 18.

GLYCOSIDATION

The stereoselective O-glycosidation of glycals is one of the most important and straightforward methods for the preparation of glycosides, which are utilized for the biologically active substances and the substrates for synthesis of medicines such as antibiotics [67]. Among glycosides the 2, 3-unsaturated glycosides [68] have a unique place and importance in carbohydrate chemistry since this unsaturation can be further functionalized. Significantly, as well as participation in simple addition reaction across the glucal double bond, the presence of a good leaving group at C-3 facilitate S_N2 reactions allowing for the introduction of a wide variety of nucleophiles at C-1 of the sugar nucleus with concomitant migration of the double bond [69]. Lewis acid-catalyzed allylic rearrangement of glycols is well known as the Ferrier reaction and widely employed to obtain the 2,3-unsaturated glycosides. Different reagents such as, boron trifluride-ether [70,71], $SnCl_4$ [72], clay catalyst montmorillonite K-10 [73], DDQ [74], $BiCl_3$ [75], N-iodosuc cinimide [76], and iodonium dicollidinium perchlorate have been introduced for the Ferrier rearrangement under mild conditions [77]. The ability of several Lewis acid catalysts; $LiC1O_4$, $LiBF_4$, BF_3-Et_2O, $SnCl_4$, $InCl_3$, $TaCl_s$ and $LnCl_3$ was also examined for the Ferrier rearrangement of 3,4,6-tri-4-acetyl D-glucal with selected alcohols; the best result was achieved using $InC1_3$ [78]. Therefore, the introduction of new effective and environmentally friendly glycosidation method have attracted considerable attention in current synthetic organic chemistry related to both biomolecules and functional materials [79].

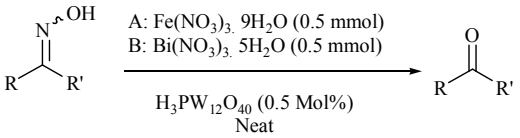
Potassium dodecatungstocobaltate ($K_5CoW_{12}0_{40}.3H_2O$) has been applied in glycosidation of **1** with some alcohols [80]. Tri-O-acetyl-n-glucal **1** (1.0 mmol) was treated with benzyl alcohol (1.5 mmol) and $K_5CoW_{12}0_{40}.3H_2O$ (0.1 mmol) in CH_3CN, CH_2Cl_2, benzene or Et_20 at ambient temperature to give the benzyl 2,3-unsaturated glycopyranoside **10**. Acetonitrile was shown to be superior to the other solvents examined. The reaction was extended to other alcohols (**3-7**) under such conditions (Table 19). The corresponding 2,3-unsaturated glycosides produce in α-anomer as the major products. $K_5CoW_{12}0_{40}.3H_2O$ can be reused several times without loss of activity by filtering the catalyst, washing with acetone, drying and immediately reusing.

Mechanistically, since potassium dodecatungstocobaltate, $K_5CoW_{12}O_{40}.3H_2O$, is apparently a perfect outer sphere one-electron oxidant due to the presence of a sheet of chemically inert oxygen atoms, which protect the central ion from undesired inner-sphere substitution reactions," this glycosidation reaction probably proceeds *via* a one-electron transfer with the initial formation of the radical cation **a** and the allylic oxonium intermediate **b** as shown in Scheme 9. The possibility of a concerted electron transfer mechanism was strongly supported by a large decrease of the reaction rate upon addition of a small amount of acrylonitrile or 2,6-di-tert-butylphenol as a radical scavenger.

ESTERIFICATION OF MANDELIC ACID

Esterification of mandelic acid is important from different aspects. The esters are employed as precursors for the synthesis of a number of medicines and pesticides. They also show repellent effect against mosquitoes of certain esters (methyl, ethyl, isopropyl, butyl, isobutyl and hexyl) of dl-mandelic acid [81]. There are a few methods for preparation of

Table 18. Oxidation of Oximes Using $Fe(NO_3)_3.9H_2O$ (Method A) or $Bi(NO_3)_3.5H_2O$ (Method B) at 40-45 °C under Solvent-Free Conditions Catalyzed by $H_3PW_{12}O_{40}$



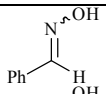
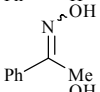
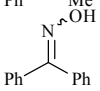
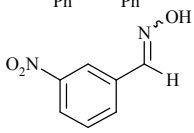
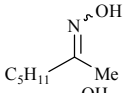
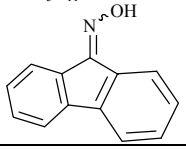
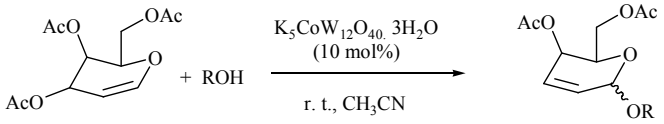
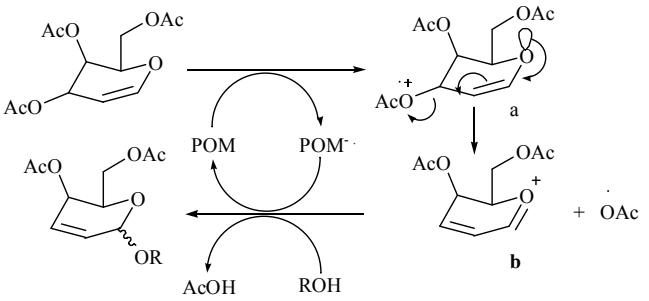
Entry	Oxime	Method	Time (min)	Yield (%)
1		A	10	95
		B	10	93
2		A	15	91
		B	10	85
3		A	10	90
		B	10	91
4		A	120	45
		B	120	67
5		A	10	83
		B	20	86
6		A	60	87
		B	60	78

Table 19. Glycosidation of **1** with Several Alcohols and Phenols by $K_5CoW_{12}O_{40}.3H_2O$



1 **2-9** **10-17**

Entry	ROH	Product	Time (h)	Yield [a] (%)	α: β[b]
1	$PhCH_2OH$ **(2)**	**10**	0.16	95	6:1
2	Cyclohexyl-OH **(3)**	**11**	48	93	9:1
3	*m*-MeO-C_6H_4-CH_2OH **(4)**	**12**	1	95	7:1
4	*o*-NO_2-C_6H_4-CH_2OH **(5)**	**13**	12	90	9:1
5	MeOH **(6)**	**14**	0.16	2	6:1
6	EtOH **(7)**	**15**	0.25	3.5	6:1
7	*p*-Cl-C_6H_4-OH **(8)**	**16**	24	0	-
8	*p*-Me-C_6H_4-OH **(9)**	**17**	24	0	-



Scheme 9

mandelates in literature. Sulfuric acid [82], 2,2-dimethoxypropane and sulfuric acid [83a], thionyl chloride [83b], ferric sulfate [83c], sodium hydrogen carbonate [83d] and TiO_2/SO_4^{2-} [83e] have been used as catalysts in direct esterification of mandelic acid with alcohols. However, some of these procedures are not entirely satisfactory and suffer from one or more of the following drawbacks such as corrosivity of the strong acids, tedious work up, low yields, long reaction times and side reactions such as carbonization, oxidation, etherification, etc.

Potassium dodecatungstocobaltate ($K_5CoW_{12}O_{40}.3H_2O$) has been used as an effective and reusable catalyst for direct esterification of mandelic acid [84]. The catalytic esterification of mandelic acid with several alcohols in the presence of catalytic amount of $K_5CoW_{12}O_{40}.3H_2O$ (0.025 mmol) was performed to proceed the corresponding mandelates in good to excellent yields (Table 20).

TETRAHYDROPYRANYLATION AND DE-TETRAHYDROPYRANYLATION OF ALCOHOLS

The importance of selective introduction and removal of protecting groups in organic synthesis is well established. Tetrahydropyranylation is one of the most frequently used methods for the protection of hydroxyl groups in synthetic organic chemistry, in particular natural product chemistry, because of its easy installation, general stability to most non-acidic reagents, and easy removal under mild acidic conditions [27b].

A wide variety of catalysts have already been applied to the tetrahydropyranylation of alcohols and phenols, and their detetrahydropyranylation including the use of protic acids [85], Lewis acids [86a] ion exchange resins (amberlyst H-15, Dowex SOW-X8 [86b], Nafion-H), bentonitic earth [86c], organotin phosphate condensates [86d], triphenylphosphine dibromide (PPh_3Br_2) [86e] and 2,3-diehloro-5,6-dicyano *p*-benzoquinone (DDQ) [86f]. However, some of these procedures suffer due to the use of expensive and toxic reagents, high temperatures, strongly acidic conditions or formation of considerable amounts of side products. It is reported that $K_5CoW_{12}O_{40}.3H_2O$ is an excellent, effective and a reusable catalyst for tetrahydropyranylation and deprotection of tetrahydropyranyl ethers to their parent alcohols [87]. As shown in Table l, the treatment of a series of alcohols with 3, 4-dihydro-2H-pyran in the presence of only 0.01 mmol of the catalyst in acetone at room temperature, afforded the corresponding tetrahydropyranyl ethers from low to excellent yields.

This protocol has been also applied for the protection of phenols the reactions proceeded slowly and the corresponding tetrahydropyranyl ethers were obtained in low yields (Table 21). Deprotection of tetrahydropyranyl ethers in the presence of catalytic amounts of $K_5CoW_{12}O_{40}.3H_2O$ has been also studied. As it is evident from the results summarized in Table 22, the reactions proceeded well at room temperature and the original alcohols were isolated in excellent yields [87].

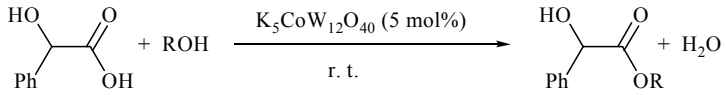
RING OPENING OF EPOXIDES

Aminolysis

Aminolysis of epoxides is an excellent synthetic tool for construction of β-amino alcohols and have been well exploited for the synthesis of pharmacologically interesting compounds [88]. A wide variety of catalysts have already been applied to the aminolysis of epoxides including $Ti(O\text{-}i\text{-}Pr)_4$ [89a], metal triflates [89d], diisopropoxyaluninum trifluoroacetate [89e], $TaCI_5$ [89f], $CeCI_3$ [89g]. However, some of the drawbacks of these methods are the long reaction times, the use of large amounts of expensive catalysts and low chemo-regio and stereo-selectivity.

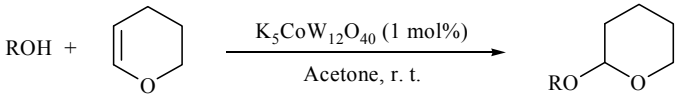
$K_5COW_{12}O_{40}.3H_2O$ has been used as an effective catalyst for aminolysis of epoxides [90] and ring opening of epoxides occurs with high regioselectivity to give β-amino alcohols

Table 20. Esterification of Mandelic Acid with Alcohols Catalyzed by $K_5CoW_{12}O_{40}.3H_2O$



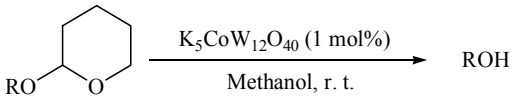
Entry	ROH	Temp.(°C)	Time (h)	Yield (%)
1	CH_3OH	Reflux	0.75	95
2	C_2H_5OH	Reflux	1.5	95
3	$CH_3(CH_2)_3OH$	80	2.5	94
6	$CH_3(CH_2)_4OH$	80	3.5	95
7	$CH_3(CH_2)_6OH$	80	4	100
8	$CH_3(CH_2)_7OH$	80	4	85
9	Cyclohexanol	80	4	80
10	$PhCH_2OH$	48	1	95

Table 21. Tetrahydropyranylation of alcohols catalyzed with $K_5CoW_{12}O_{40}.3H_2O$



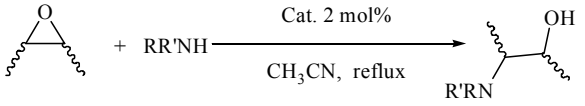
Entry	ROH	Time (min)	Yield (%)
1	$2\text{-}NO_2C_6H_4CH_2OH$	15	75
2	$4\text{-}ClC_6H_4CH_2OH$	5	97
3	$2\text{-}MeOC_6H_4CH_2OH$	5	95
4	$C_6H_5CH_2CH_2CH_2OH$	5	98
5	$C_6H_5CH(OH)CH_3$	10	95
6	$C_6H_5CH(OH)COC_6H_5$	10	80
7	$CH_3(CH_2)_6CH_2OH$	5	86
8	a-Tetralol	5	100
9	(-)-Menthol	15	82
10	Adamantanol	15	60

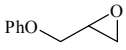
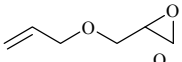
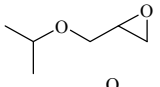
Table 22. Deprotection of THP-ethers of alcohols catalyzed by $K_5CoW_{12}O_{40}.3H2O$



Entry	ROH	Time (h)	Yield (%)
1	Furfuryl alcoholTHP	1.5	100
2	4-C1$C_6H_4CH(OTHP)CH_3$	0.75	100
3	4-$MeOC_6H_4CH_2OTHP$	1	100
4	$C_6H_SCH(OTHP)C_6H_5$	1.5	95
5	4-$N0_2C_6H_4CH_2OTHP$	0.75	95
6	$CH_3(CH_2)_5CH_2OTHP$	2	100

Table 23. Aminolysis of Epoxide Catalyzed by $K_5COW_{12}O_{40}.3H_2O$



Entry	Epoxide	Amine	Time (h)	Yield (%)
1		$PhNH_2$	3	93
2		4-$BrC_6H_4NH_2$	3.25	93
3		4-$EtC_6H_4NH_2$	3	94
4		4-$MeOC_6H_4NH_2$	3.75	91
5		4-Methylpiperidine	5	87
6		4-$MeC_6H_4NH_2$	2	98
7		$PhNH_2$	4.5	93
8		4-$BrC_6H_4NH_2$	3.5	98
9		4-$EtC_6H_4NH_2$	3	94
10		4-$MeOC_6H_4NH_2$	2.5	99

(Table 23). The reaction rates depend on the structure of the amines and the epoxides. With non-aromatic epoxides, the primary carbon is much more reactive towards amines than the secondary one.

Reaction with Carbonyl Compounds

Acetals are among the most popular protecting group for carbonyl compounds [27b]. In addition, they are useful intermediates, particularly in carbohydrate [91a] and steroid [91b] chemistry and are very well suited for GC, GLC and mass spectral analysis of diols [91c]. In the pharmaceutical [91d], phytopharmaceutical, fragrance [91e] and lacquer [91f] industries, acetals are used both as intermediates and as end products. Reagents such as anhydrous copper sulfate [91c] , zeolite [92a], $TiCI_3(OTf)$ [92b], $RuC1_3$ [92c], bismuth (III) salts [92d] and iron (III) trifluoroacetate [92e] have been used for this purpose. Most of the Lewis acids failed to give the desired products. The similar reaction with both $FeCl_3$ [93a] and Me_3SiCI [93b] gives the corresponding halohydrins, while $SnC1_4$ and $TiC1_4$ [93c] produce little or no product. BF_3-OEt_2 has been also successfully used for the conversion of ethylene and propylene oxides to their corresponding 1, 3-dioxolanes in the presence of different carbonyl compounds [93c].

Ammonium dodecatungstocerate $[(NH_4)_3CeW_{12}O_{38}]$ has been recently applied as an efficient, reusable and heterogeneous catalyst for the conversion of epoxides to their 1,3-dioxolanes with acetone [94].

OXIDATION OF HYDROCARBONS

Numerous hydrocarbon oxidation systems based on metalloporphyrin derivatives that mimic the acidity of cytochrome P-450 have been reported [95]. However, degradation of the common synthetic metalloporphyrins in the presence of strong oxidizing agents has prevented their practical applications. Heteropolyoxametalates as oxidatively stable inorganic porphyrins have received much attention as homogeneous catalysts because of their ability to utilize environmentally and economically acceptable hydrogen peroxide as oxygen donor [96]. Catalytic oxidation with hydrogen peroxide has been limited to polyoxometalates containing only electron-poor metals in d° state [97], or disubstituted polyoxometalates with general formula $[WM_2(ZnW_9O_{39})_2]$, where M stands for Mn^{2+}, Pb^{2+}, or Pt^{2+} [98].

Zinc containing polyoxometalate $\{[(n\text{-}Bu)_4N]_5PZnMo_2W_9O_{39}.3H_2O\}$ has been applied as a catalyst for the epoxidation of alkenes and Some polyoxometalates such as $[(n\text{-}Bu)_4N]_5PZnMo_2W_9O_{39}.3H_2O$, $[(n\text{-}Bu)_4N]_5PCoMo_2W_9O_{39}.5H_2O$, $(n\text{-}Bu)_4N]_4PMnMo_2W_9O_{39}.6H_2O$, $[(n\text{-}Bu)_4N]_4PFeMo_2W_9O_{39}.5H_2O$, α-$K_7PMo_2W_9O_{39}.3H_2O$ have been investigated for epoxidation of cyclooctene with H_2O_2 (30%).Among these catalysts only $[(n\text{-}Bu)_4N]_5PZnMo_2W_9O_{39}.3H_2O$ has shown superior activity for this epoxidation reaction and the desired epoxide has been formed in 90% (GC) in the reaction mixture. However, zinc containing polyoxometalate $\{[(n\text{-}Bu)_4N]_5PZnMo_2W_9O_{39}.3H_2O\}$ has been used for epoxidation of structurally different alkene and hydroxylation of alkyl-aromatics with promising selectivity as shown in Table 24 in a solution of H_2O_2 (30%) [99].

OXIDATION OF ALCOHOLS TO CARBONYL COMPOUNDS

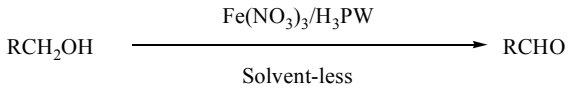
Carbonyl compounds in the fine chemicals industry are precursors with wide applicability from drugs to fragrances. The oxidation of alcohols to carbonyl products is an important transformation in organic chemistry [100], which has received most attention over the years, especially the search for versatile and selective reagents in catalytic applications [101]. Methods which are available for selective oxidation of alcohols to the corresponding carbonyl compounds are not free from some disadvantages and there still exist a need for new methods. The main requirements are simplicity of the method, selectivity, in particular with regard to over-oxidation of carbonyl compounds to carboxylic acids, effectiveness and mildness of the reaction conditions. Thus, most of the current industrial oxidation processes are outmoded and are used polling oxidants in solution like the heavy metals Cr (VI) or Mn (VI), and industries are under pressure to replace them with catalytic processes using clean oxidants, such as oxygen, H_2O_2 and other inexpensive and environmentally friendly oxidants.

Metal nitrates supported on various inorganic supports have been used as oxidizing agents. Ferric nitrate supported on

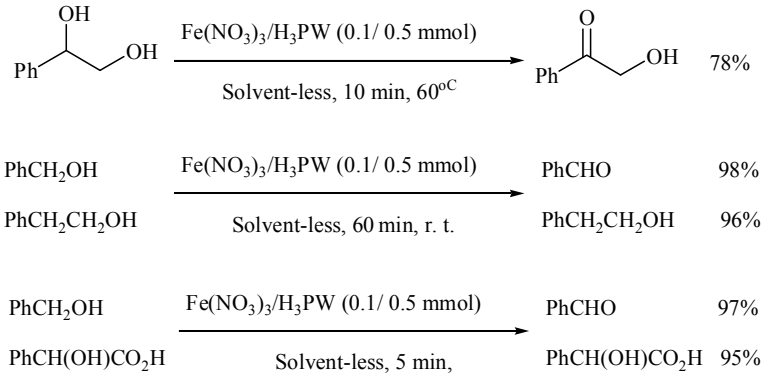
Table 24. Oxidation of Various Hydrocarbons with a Solution of H_2O_2 (30%) Catalyzed by $[(n\text{-}Bu)_4N]_5PZnMo_2W_9O_{39}.3H_2O$

Entry	Substrate	Product	Time (h)	Yield (%)
1	Cyclooctene	Cyclooctene oxide	4	90
2	Styrene	Styrene oxide	24	54
		Acetophenone		13
3	1-Octene	1-Octene oxide	24	24
4	R-(+)-Limonene	1, 2-Limonene oxide	3	80
5	Ethylbenzene	Acetophenone	24	38
6	Diphenylmethane	Benzophenone	24	26

Table 25. Oxidation of Various Alcohols with Ferric Nitrate Nonahydrate Catalyzed by the Tungstophosphoric Acid (H_3PW)

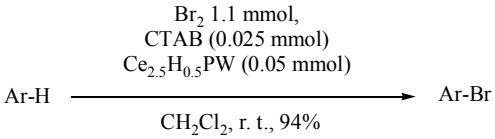


Entry	Alcohol	Sub./H3PW/$Fe(NO_3)_3$	Time (min)	Yield (%)
1	$PhCH_2OH$	1: 0.1: 0.5	5	95
2	$4\text{-}MeOC_6H_4CH_2OH$	1: 0.1: 0.5	10	97
3	$2\text{-}NO_2C_6H_4CH_2OH$	1: 0.1: 0.625	15	96
4	Ph_2CHOH	1: 0.1: 0.625	5	95
5	$(D)\text{-}PhCH(OH)CO_2H$	1: 0.1:0.75	10	93
6	PhCH(OH)C(O)Ph	1: 0.1: 1	60	95
7	$Me(CH_2)_6CHOH$	1:0.1:0.625	24 h	0
8	$Me(CH_2)_5CH(OH)Me$	1: 0.1: 0.625	3 h	92
9	Norboreneol	1: 0.1: 0.625	15	94



Scheme 10

Table 26. Bromination of Aromatic Compounds with Bromine in the Presence of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ CTAB System at Room Temperature in CH_2Cl_2



Entry	Aromatic compound	Product	Time (min)	Yield (%)
1	PhOH	4-Bromophenol	Im.	94
2	2-Methoxyphenol	4- Bromo -2-methoxyphenol	Im.	96
3	2-Chlorophenol	4- Bromo-2-chlorophenol	15	96
4	2,6-Dichlorophenol	4-Bromo-2, 6-dichlorophenol	30	88
5	Anisole	4- Bromoanisol	10	97
6	Anthracene	9-Bromoanthracene	Im.	90
7	Aniline	4-Bromoaniline	Im.	43
8	2-Chloroaniline	4-Bromo-2-chloroaniline	Im.	91
9	N,N-dimethylaniline	4-Bromo-N,N-dimethylaniline	10	97
10	Acetanilide	4-Bromoacetanilide	5	98

K10-clay (Clayfen) [102a], Ferric nitrate supported on silica gel (Silfen) [102b,c], and ferric nitrate mixed with HZSM-5 zeolite (Zeofen) have been successfully employed for the oxidation of various alcohols in solution and also in the absence of solvent under microwave irradiation [103].

It is reported that the catalytic amounts of tungstophosphoric acid ($H_3PW_{12}O_{40}$) catalyzes oxidation with safe and commercially available ferric nitrate noanahydrate for the simple, swift and selective oxidation of a wide variety of primary, secondary, and benzylic alcohols into their corresponding carbonyl compounds under mild and solvent-less conditions (Table 25) [104]. Chemoselectivity of the method has been studied and the results are demonstrated by Scheme 10.

REGIOSELECTIVE BROMINATION OF AROMATIC COMPOUNDS

Bromoarenes are widely used intermediates of commercial importance [105]. Many reagents such as solid brominating agents [106], Br_2-Lewis acids and Br_2-supported [107], reported in the literature for the electrophilic bromination of aromatic compounds.

Cesium salt of the heteropoly acid ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$) in the presence of cetyltrimethylammonium bromide has been used for highly controlled regioselective bromination of phenols and some aromatic compounds with molecular bromine [108]. The results are tabulated in Table 26.

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REFERENCES

[1] a) P.T. Anastas, J.C. Warner, Green Chemistry, Theory and Practice, Oxford University Press, 1998; b) J.H. Clark, Green Chemistry 1 (1999) 1.

[2] V. Kozhevnikov, in: E. Derouane (Ed.), Catalysts for Fine Chemical Synthesis, Catalysis by Polyoxometalates 2, Wiley, New York, 2002.

[3] S. Nakato, M. Kimura, T. Okuhara, Chem. Lett. (1997) 389.

[4] M. Kimura, T. Nakato, T. Okuhara, Appl. Catal. A Gen. 165 (1997) 227.

[5] T. Nakato, Kimura, M. Nakata, S. Okuhara, T. Langmuir 14 (1998) 319.

[6] REF

[7] J.H. Clark, Chem. Rev. 80 (1980) 429.

[8] R.A. Sheldon, Chirotechnologies, Industrial Synthesis of Optically Active Compounds; Dekker Publishing: New York, 1993.

[9] E. Emori, T.H. Sasai, M. Shibasaki, J. Am. Chem. Soc. 120 (1998) 4043.

[10] a) S. Kanemasa, Y. Oderaotoshi, E. Wada, J. Am. Chem. Soc. 121 (1999) 8675; b) M. Bandini, P.G. Cozzi, M. Giacomini, P. Melchiorre, S. Selva, A. Umani-Ronchi, J. Org. Chem. 67 (2002) 3700; c) N. Srivastava, K. Banic, J. Org. Chem. 68 (2003) 2109; d) K. Subbareddy, A. Sudalai, B.C. Benicewicz, Tetrahedron Lett. 42 (2001) 3791; e) J.S. Yadav, B.V.S. Reddy, G. Baishya, J. Org. Chem. 68 (2003) 7098; f) B.C. Ranu, S.S. Dey, A. Hajra, Tetrahedron 59 (2003) 2417; g) T.C. Wabnitz, J.B. Spencer, Org. Lett. 5 (2003) 2141; h) T.C. Wabnitz, J. Yu, J.B. Spencer, Synlett (2003) 1070.

[11] H. Firouzabadi, N. Iranpoor, A.A. Jafari, Synlett (2005) 299.

[12] H. Heaney, in: B.M. Trost, I. Fleming (Eds.), Comprehensive Organic Synthesis Pergamon Press, Oxford, 1991, pp. 733-752.

[13] a) T. Harada, T. Ohno, S. Kobayashi, T. Mukaiyama, Synthesis (1991) 1216; b) A. Kawada, S. Mitamura, S. Kobayashi, Synlett (1994) 545; c) S. Pivsa-Art, K. Okura, M. Miura, S. Murata, M. Nomura, J. Chem. Soc. PerkinTrans1 13 (1994) 1703; d) A. Kawada, S. Mitamura, S. Kobayashi, J. Chem. Soc. Chem. Commun. (1996) 183; e) F. Effenberger, J.K. Eberhard, A.H. Maier, J. Am. Chem. Soc. 118 (1996) 12572; f) J. Nishikido, H. Nakajima, T. Saeki, A. Ishii, K. Mikami, Synlett (1998) 1347; g) S. Repichet, C.L. Roux, J. Dubac, J.R. Desmurs, Eur. J. Org. Chem. (1998) 2743; h) H. Nakano, T. Kitazume, Green Chem. (1999) 179; i) J. Matsuo, K. Odashima, S. Kobayashi, Synlett (2000) 403.

[14] a) A.G.M. Barrett, N. Bouloc, D.C. Braddock, D. Chadwick, D.A. Hendersona, Synlett (2002) 1653; b) G. Bartoli, M. Bosco, E. Marcantoni, M. Massaccesi, S. Rinaldi, Sambri, L. Tetrahedron Lett. 43 (2002) 6331.

[15] a) Q.L. Wang, Y. Ma, X. Ji, H. Yan, Q. Qiu, J. Chem. Soc. Chem. Commun. (1995) 2307; b) J. Kaur, I.V. Kozhevnikov, Chem. Commun. (2002) 2508; c) B. Chiche, A. Finiels, C. Gauthier, P. Geneste, J. Org. Chem. 51 (1986) 2128; d) B.C. Ranu, K. Ghosh, U. Jana, J. Org. Chem. 61 (1996) 9546.

[16] a) H. Firouzabadi, N. Iranpoor, F. Nowrouzi, Tetrahedron 60 (2004) 10843; b) H. Firouzabadi, N. Iranpoor, F. Nowrouzi, Tetrahedron Lett. 44 (2003) 5343.

[17] a) W.R. Jackson, H.A. Jacobs, B.R. Matthews, G.S. Jayatilake, K.G. Watson, Tetrahedron Lett. 31 (1990) 1447; b) T. Ziegler, B. Horsch, F. Effenberger, Synthesis (1990) 575; c) P. Zandbergen, J. Brussee, A. Van der Gen, C.G. Kruse, Tetrahedron Asymmetry 3 (1992) 769.

[18] a) R.J.H. Gregory, Chem. Rev. 99 (1999) 3649; b) H. Deng, M.P. Ister, M.L. Snapper, A.H. Hoveyda, Angew. Chem. Int. Ed. 41 (2002) 1009; c) S.K. Tian, R. Hong, L. Deng, J. Am. Chem. Soc. 125 (2003) 9900; d) N. Azizi, M.R. Saidi, J. Organometallic Chem. 688 (2003) 283; e) Z. Wang, B. Fetterly, J.G. Verkade J. Organometallic Chem. 646 (2002) 161.

[19] a) M. Bandini, P.G. Cozzi, P. Melchiorre, A.V. Ronchi, Tetrahedron Lett. 42 (2001) 3041; b) M. Curini, F. Epifano, M.C. Marcotullio, O. Rosati, M. Rossi, Synlett (2002) 315; c) F. Chen, X. Feng, B. Qin, G. Zhang, Y. Jiang, Synlett (2003) 558; d) Y. Shen, X. Feng, Y. Li, G. Zhang, Y. Jiang, Tetrahedron 59 (2003) 5667; e) Y. Shen, X. Feng, Y. Li, G. Zhang, Y. Jiang, Synlett (2002) 793; f) S.S. Kim, D.W. Kim, G. Rajagopal, Synthesis 2 (2004) 213; g) H.S. Wilkinson, P.T. Grover, C.P. Vandenbossche, R.P. Bakale, N.N. Bhongle, S.A. Wald, C.H. Senanayake, Org. Lett. 3 (2001) 553.

[20] H. Firouzabadi, N. Iranpoor, A.A. Jafari, J. Organometallic Chem. 690 (2005) 1556.

[21] a) N. Bagget, In Comprehensive Organic Synthesis; series Ed. by D. Barton, W.D. Ollis, vol. Ed. Stoddart J. F.; Pergaman, Oxford, 1979, P. 799.

[22] M.B. Smith, J. March, Advanced Organic Chemistry, 5th Edition, Wiley-Interscience, New York, 2001, pp. 479-480.

[23] a) T. Ooi, H. Ichikawa, Y. Itagaki, K. Maruoka, Heterocycles 52 (2000) 575; b) K. Manab, S. Limura, X. Sun, S. Kobayashi J. Am. Chem. Soc. 124 (2002) 11971.

[24] a) N. Iranpoor, E. Mottaghinejad, Synth. Commun. 25 (1995) 2253; b) P. Salehi, N. Iranpoor, F. Kargar Behbahani, Tetrahedron 54 (1998) 943.

[25] a) J.S. Bajwa, X. Jiang, J. Slade, K. Prasad, O. Repic, T. J. Blacklock, Tetrahedron Lett. 43 (2002) 6709; b) X. Jiang, J.S. Bajwa, J. Slade, K. Prasad, O. Repic, T.J. Blacklock, Tetrahedron Lett. 43 (2002) 9225.

[26] H. Firouzabadi, N. Iranpoor, A.A. Jafari, J. Molecular Cat. A Chemical 227 (2005) 97.

[27] a) S.G. Wilkinson, in: J.F. Stoddart (Ed.), In Comprehensive Organic Chemistry, Vol. 1; Pergamon Press: Oxford, 1979, Chap 4.1, 579-706; b) T.W. Green, P.G.M. Wuts, In Protective Groups in Organic Synthesis, 3rd Ed.; John Wiley & Sons: New York, 1999.

[28] H. Firouzabadi, N. Iranpoor, A.A. Jafari, Tetrahedron Lett. 46 (2005) 2683.

[29] A.B. Smith, S.M. Condon, J.A. McCauley, Acc. Chem. Res. 31 (1998) 35.

[30] P.C. Bulman Page, J.C. Prodger, D. Westwood, Tetrahedron 49 (1993) 10355.

[31] J. Taleiwa, H. Horiuchi, S. Vemura, J. Org. Chem. 60 (1995) 4039.

[32] a) S. Muthusamy, S.A. Babu, C. Gunanathan, Tetrahedron Lett. 42 (2001) 359; b) L.F. Tietze, B. Weigand, C. Wulff, Synthesis (2000) 69.

[33] a) H. Firouzabadi, N. Iranpoor, B. Karimi, H. Hazarkhani, Synlett (2000) 263; b) H. Firouzabadi, N. Iranpoor, B. Karimi, Synlett (1999) 319; c) H. Firouzabadi, N. Iranpoor, B. Karimi, Synthesis (1999) 58.

[34] a) R. Vijaya Anand, P. Saravanan, V.K. Singh, Synlett (1999) 415.

[35] a) F. Bellesia, M. Boni, F. Ghelf, U.M. Pagnoni, Tetrahedron 49 (1993) 199; b) G.K. Jnaneshwara, N.B.

Barhate, A. Sudalai, V.H. Deshpande, A.S. Gajare, M.S. Shingare, R. Sukumar, J. Chem. Soc. Perkin Trans. 1 (1998) 965.

[36] H. Firouzabadi, N. Iranpoor, K. Amani, Synthesis (2002) 59.

[37] C.A Bruynes, T.K. Jurriens, J. Org. Chem. 47 (1982) 3966.

[38] a) K. Tanaka, F. Toda, Chem. Rev. 100 (2000)1025; b) H. Firouzabadi, N. Iranpoor, S. Sobhani, Tetrahedron Lett. 43 (2002) 3653; c) H. Firouzabadi B. Karimi, Synth. Commun. 23 (1993) 1633; d) H. Firouzabadi, A. R. Sardarian, Z. Khayat, B. Karimi S. Tangestaninejad, Synth. Commun. 27 (1997) 2709; e) B. Karimi, B. Golshani, J. Org. Chem. 65 (2000) 7228.

[39] H. Firouzabadi, N. Iranpoor, K.Amani, F. Nowrouzi, J. Chem. Soc. Perkin Trans. 1 (2002) 2601.

[40] M.H. Habibi, S. Tangestaninejad, I. Mohammadpoor-Baltork, V. Mirkhani, B. Yadollahi Tetrahedron Lett. 42 (2001) 6771.

[41] a) W. Steglich, G. Höfle, Angew. Chem. Int. Ed. Engl., 8 (1969) 981; b) G. Höfle, W. Steglich, H. Vorbrüggen, Angew. Chem. Int. Ed. Engl. 17 (1978) 569.

[42] (a) K.K. Chauhan, C.G. Frost, L. Love, D. Waite, Synlett (1999) 1743; b) K. Ishihara, M. Kubota, H. Kurihara H. Yamamoto, J. Org. Chem. 61 (1996) 4560; c) A. Orita, C. Tanahashi, A. Kakuda, J. Otera Angew. Chem. Int. Ed., 39 (2000) 2877; d) M.D. Carrigan, D. A. Freiberg, R.C. Smith, H.M. Zerth R.S. Mohan, Synthesis (2001) 2091.

[43] H. Firouzabadi, N. Iranpoor, F. Nowrouzi, K. Amani, Chem. Commun. (2003) 764.

[44] a) M.H. Habibi, S. Tangestaninejad, V. Mirkhani, B. Yadollahi Monatshefte Fur Chemie 133 (2002) 323; b) M.H. Habibi, S. Tangestaninejad, V. Mirkhani, B. Yadollahi Tetrahedron 57 (2001) 8333.

[45] K.S. Kochhar, B.S. Bal, R.P. Deshpande, S.N. Rajadhyaksha, H.W. Pinnick, J. Org. Chem. 48 (1983) 1765.

[46] a) B.M. Trost, C.B. Lee, J.M. Weiss, J. Am. Chem. Soc. 117 (1995) 7247; b) N. Deka, D.J. Kalita, R. Borah, J. C. Sharma, J. Org. Chem. 62 (1997) 1563; c) K.L. Chandra, P. Saravanan, V.K. Singh, Synlett (2000) 359; d) B. Karimi, H. Seradj, G.R. Ebrahimian, Synlett (2000) 623; e) N. Sumida, K. Nishioka, T. Sato, Synlett (2001) 1921; f) B.M. Trost, C.B. Lee, J. Am. Chem. Soc. 123 (2001) 3671; g) S.C. Roy, B. Banerjee, Synlett (2002) 1677.

[47] a) Sandberg, M. Sydnes, L.K. Tetrahedron Lett. 39 (1998) 6361; b) M. Sandberg, L.K. Sydnes, Org. Lett. 2 (2000) 687.

[48] H. Firouzabadi, N. Iranpoor, F. Nowrouzi, K. Amani Tetrahedron Lett. 44 (2003) 3951.

[49] S.M. Dirk, E.T. Mickelson, J.C. Henderson, J.M. Tour, Org. Lett. 2 (2000) 3405.

[50] a) K.S. Webb, V. Seneviratne, Tetrahedron Lett. 36 (1995) 2377; b) S. Tollari, D. Vergani, S. Banfi, F. Porta, J. Chem. Soc. Chem. Commun. (1993) 442; c) S. Sakaue, T. Tsubakino, Y. Nishiyama, Y. Ishii, J. Org. Chem. 58 (1993) 3633.

[51] a) Z. Zhu, J.H. Espenson, J. Org. Chem. 60 (1995) 1326; b) S. Sakaue, T. Tsubakino, Y. Nishiyama, Y. Ishii, J. Org. Chem. 58 (1993) 3633.

[52] a) J. Muzart, Synthesis (1995) 1325.

[53] H. Firouzabadi, N. Iranpoor, F. Nowrouzi, K. Amani, Green Chem. 3 (2001) 131.

[54] N.D. Cheronis, J.B. Entrikin, Identification of Carbonyl Compounds, Interscience: New York, 1963.

[55] H.M.S. Kumar, T.P. Reddy, J.S. Yadav, Synthesis (1999) 586.

[56] P.R. Dave, F. Forshar, J. Org. Chem. 61 (996) 8897.

[57] M.E. Enikaki, X.N. Stamplos, T.A. Charalambis, C.C. Karapostolon, Tetrahedron 53 (1997) 747.

[58] S. Negi, M. Matsukura, M. Mizuno, K. Miyake, Synthesis (1996) 991.

[59] J.T. Pulkkiner. J.J. Vepsalainen, J. Org. Chem. 61 (1996) 8604.

[60] J.K. Whitesell, M.A. Whitesell, Synthesis (1983) 54.

[61] a) W. Chrisman, M.J. Blankinship, B. Taylor, C.E. Harris, Tetrahedron Lett. 42 (2001) 4775; b) A.R. Hajipour, N. Mahboubhgah, Org. Prep. Proced. Int. 31 (1999) 112.

[62] A. Corsaro, U. Chiacchio, V. Pistara, Synthesis (2001) 1903.

[63] J.G. Lee, J.P. Hwang, Chem. Lett. 7 (1995) 507.

[64] H.M. Meshram, G.S. Reddy, D. Srinivas, J.S. Yadav, Synth. Commun. 28 (1998) 2593.

[65] a) B.A. Nattier, K.J. Eash, R.S. Mohan, Synthesis (2001) 1010; b) B. Tamami, A. Kiasat, Synth. Commun. 30 (2000) 4129; c) A. McKillop, J.D. Hunt, E.C. Taylor, R.D. Naylor J. Am. Chem. Soc. 93 (1971) 4918; d) J.W. Bird, D.G.M. Diaper, Can. J. Chem. 47 (1969) 145.

[66] H. Firouzabadi, N. Iranpoor, K. Amani, Synthetic Commun. 34 (2004) 3587.

[67] N.R. Williams, J.D. Wander The Carbohydrates Chemistry and Biochemistry; Academic: New York, 1980, p. 761.

[68] J. Ramnauth, O. Poulin, S.P. Rakhit, S.P. Maddaford, Org. Lett. 3 (2001) 2013.

[69] P. Collins, R. Ferrier, Monosaccharides: their Chemistry and their Roles in Natural Products; Wiley: Chichester (1995).

[70] a) K. Toshima, K. Tatsuta, Chem. Rev. 93 (1993) 1503; b) D.E. Levy, C. Tang, The Chemistry of C-Glycosides; Pergamon: New York , 1995.

[71] P. KlaOke, D. Springer, J. Thiem, Liebigs Ann Chem. (1991) 509.

[72] P. Bhate, D. Horton, W. Priebe, Carbohydr. Res. 144 (1985) 331.

[73] G. Matsuo, M. Kakata, S. Matsumura, Chem. Commun. (1996) 1379.

[74] K. Toshima, T. Ishizuka, G. Matsuo, M. Nakata, M. Konoshita J. Chem. Soc. Chem. Commun. (1993) 704.

[75] N.R. Swamy, Y. Venkateswarlu, Synthesis 5 (2002) 598.

[76] B. Fraser-Reid, R.J. Madsen, Org. Chem. 60 (1995) 3851.

[77] J.C. Lopez, B. Fraser-Reid, J. Chem. Soc. Chem. Commun. (1992) 94.

[78] B.B. Babu, K.K. Balasubramanian, Tetrahedron Lett. 41 (2000) 1271.

[79] a) R.R. Schmidt, Angew. Chem. Int. Ed. Engl. 25 (1986) 212; b) G.J. Boons Tetrahedron 52 (1996) 1095.

[80] E. Rafiee, S. Tangestaninejad, M.H. Habibi, V. Mikhani Bioorg. Med. Chem. Lett. 14 (2004) 3611.

[81] C.N. Smith, D. Burnett, J. Econ. Entomol 42 (1949) 439. d) Piper, Hall, Wright, Ind. Eng. Chem. 43 (1951) 11.

[82] S.G. Cohen, R.M. Schultz, S.Y. Weinstein, J. Am. Chem. Soc. 88 (1966) 5315.

[83] a) P. Huszthy, J.S. Bradshaw, C.Y Zhu, R.M. Izatt, J. Org. Chem. 56 (1991) 3330; e) T. S. Jin, R.Y. Ma, Y. Li, X. Sun, T.S. Li, Synthetic Commun. 31 (2001) 2051.

[84] E. Rafiee, S. Tangestaninejad, M.H. Habibi, V. Mikhani, Bull. Korean Chem. Soc. 25 (200) 599.

[85] E.J. Corey, H. Niwa, J. Knolle, J. Am. Chem. Soc. 100 (1978) 1942.

[86] a) S. Kim, J.H. Park, Tetrahedron Lett. 28 (1987) 439; b) G.A. Olah, A. Husain, B.P. Singh, Synthesis (1983) 892; c) R. Cruz-Almanza, F.J. Perez-Felores, M. Avila, Synthetic Commun. 20 (1990) 1125; d) J. Otera, Y. Niibo, S. Chikada, H. Nozaki, Synthesis (1988) 328; e) A. Wagner, M.P. Heitz, C. Mioskovski, J. Chem. Soc. Chem. Commun. (1989) 1619; f) S. Raina, V.K. Singh, Synthetic Commun. 25 (1995) 2395.

[87] M.H. Habibi, S. Tangestaninejad, I. Mohammadpoor-Baltork, V. Mirkhani, B. Yadollahi, Tetrahedron Lett. 42 (2001) 2851.

[88] G.A. Roger, S.M. Parsons, D.C. Anderson, L.M. Nilsson, B.A. Bahr, W.D. Kornreieh, R. Kaufman, R.S. Jacobs, B. Kirtman, J. Med. Chem. 32 (1989) 1217.

[89] a) S. Sagava, H. Abe, Y.T. Hase, Inabe, J. Org. Chem. 64 (1999) 4962; b) G. Sekar, V.K. Sing, J. Org. Chem. 64 (1999) 287; c) J. Auge, F. Leroy, Tetrahedron Lett. 37 (1996) 7715; d) M. Meguro, N. Asao, Y. Yamamoto, J. Chem. Soc. Prkin Trans I (1994) 2597; e) S. Rampalli. S.S. Chaudhari. K.G. Akamanchi, Synthesis 1 (2000) 8; f) S. Chandrasekhar, T. Ramachandar, S.J. Prakash, Synthesis (2000) 1817; g) L.R. Reddy, M.A. Reddy, N. Bhanumathi, K.R. Rao, Synthesis (2001) 831.

[90] E. Rafiee, S. Tangestaninejad, M.H. Habibi, V. Mikhani, Synthetic Commun. 34 (2004) 3673.

[91] a) D.M. Clod, Chem. Rev. 79 (1979) 491; b) J.J. Brown, R.H. Lenhard, S. Brestein, J. Am. Chem. Soc. 86 (1964) 2183; c) R.P. Hanzlik, Leinwetter, J. Org. Chem. 43 (1978) 438; d) J. Wolinski, A. Czerwinska, Acta Pol. Pharm. 33 (1976) 696; e) K. Bruns, J. Conrad, A. Steigel, Tetrahedron 35

(1979) 4543; f) F.A. Meskens, Synthesis (1981) 501.

[92] a) L.W. Zatorski, P.T. Wiezchowski, Catal. Lett. 10 (1991) 211; b) N. Iranpoor, B. Zeynizadeh, J. Chem. Res. (S) (1998) 466; c) N. Iranpoor, F. Kazemi, Synthetic Commun. 28 (1998) 3189; d) I. Mohammadpoor-Baltork, H. Alian, A.R. Khosropour, Synthetic Commun. 31 (2001) 3411; e) N. Iranpoor, H. Adibi, Bull. Chem. Soc. Jpn. 73 (2000) 675.

[93] a) Kagan, B.E. Firth, N.Y. Shih, C. Boyajian, J. Org. Chem. 42 (1977) 343; b) D.J. Harvey, Res. Commun. Chem. Pathol. Pharmacol. 4 (1972) 247; c) D.S. Torok, J.J. Figueroa, W.J. Scott, J. Org. Chem. 58 (1993) 7274.

[94] V. Mirkhani, S. Tangestaninejad, B. Yadollahi, L. Alipanah, Catalysis Lett. 91 (2003) 129.

[95] B. Meunier, Chem. Rev. 92 (1992) 1411.

[96] Y. Ishii, M. Ogawa, Hydrogn Peroxide Catalyzed by Heteropoly Acids Combined with Cetylpyridinium Chloride, MYU, Tokyo, 1990.

[97] A. J. Bailey, W. P. Griffith, B. C. Parkin, J. Chem. Soc. Dalton Trans. (1995) 1833.

[98] R. Neumann, M. Gara, J. Am. Chem. Soc. 116 (1994) 5509.

[99] S. Tangestaninejad, B. Yadollahi, Chemistry Lett. (1998) 511.

[100] Comprehensive Organic Synthesis (Oxidation); in: B.M. Trost (Ed.), Pergamon; New York, 1991, vol. 7.

[101] J. Muzart, Chem. Rev. 92 (1992) 113.

[102] a) P. Laszlo, A. Cornelis, Synthesis (1985) 909; b) B. Khadilkar, S. Borkar, Synthetic Commun. 28 (1998) 207; c) M. Hirano, K. Komiya, T. Morimito, Org. Prep. Proced. Int. 27 (1995) 703.

[103] M.M. Heravi, D. Ajami, M.M. Mojtahedi, M. Ghassemzadeh, Chem. Commun. (1999) 833.

[104] H. Firouzabadi, N. Iranpoor, K. Amani, Synthesis (2003) 408.

[105] a) C. Christophersen, Acta. Chemica. Scand. 39B (1985) 515; b) A. Butler, J.V. Walker, Chem. Rev. 93 (1993) 1937.

[106] H.A. Muathen, J. Org. Chem. 57 (1992) 2740.

[107] a) K. Smith, G.A. El-Hiti, M. E.W. Hammond, D. Bahzad, Z. Li, C. Siquet, J. Chem. Soc. Perkin Trans. 1 (2000) 2745; b) J.H. Clark, J.C. Ross, D.J. Macquarrie, S.J. Barlow, T.W. Bastock, Chem. Commun. (1997) 1203; c) T.J. Oberhauser, Org. Chem. 62 (1997) 4504.

[108] H. Firouzabadi, N. Iranpoor, K. Amani, J. Mol. Cat. A Chemical 195 (2003) 289.