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Different products in the reaction of the alcohols with cyclic and acyclic 1,3-dicarbonyl compounds: $K_5CoW_{12}O_{40}$ as an electron transfer nano catalyst

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Abstract

$K_5CoW_{12}O_{40}$ was used as a highly effective catalyst for the benzylation of 1,3-dicarbonyl compounds. β-Keto enol ethers were obtained when cyclic 1,3-dicarbonyl compounds used in this conditions instead of linear ones. The present methodology offers a practical, simple, mild, environmentally friendly, and time-saving method for etherification. Very low loading of catalyst, ease of workup, ease of handling, and reusability of catalyst are other advantages of this catalyst.

Keywords: Benzylation; Etherification; β-Keto enol ethers; Nano catalyst; Polyoxometalate

Nano-sized catalysts continue to attract interest for different researcher areas due to their different physical and chemical properties when compare to bulk material. The extremely small size of the particles maximized the surface area exposed to the reactant, allowing more reactions to occur at the same time, thus speeding up the process. Catalysis by polyoxometalates and related compounds is a field of increasing importance as nano catalysts [1–3]. They are promising candidates for catalyst design due to their controllable acid and redox properties and have been actually utilized in some industrial processes [4]. As an interesting example, 12-tungstocobaltate(III), $[Co^{III}W_{12}O_{40}]^{5-}$, having $E_0 = 1.07$ V (against a normal hydrogen electrode) has been used as an oxidant both for organic and inorganic substances [5,6]. It is apparently a perfect outer-sphere oxidant because the central Co^{III} atom is protected by a sheath of chemically inert oxygen atoms, which protect the central ion from undesired inner-sphere substitution reactions. The self-exchange rate between $[Co^{III}W_{12}O_{40}]^{5-/6-}$ couples found extensive use in the catalytic application [6]. This catalyst showed excellent reactivity in our previous works [7,8] as a heterogeneous catalyst.

During the course of our studies directed towards the development of practical and environmentally friendly procedures for some important transformations, we developed the applicability of a recyclable heterogeneous catalyst, potassium dodecatungstocobaltate trihydrate, $K_5CoW_{12}O_{40}\cdot 3H_2O$ (KCoW), for the condensation reaction of alcohols with 1,3-dicarbonyl compound. This reaction offers different products related to the cyclic or linear dicarbonyl compounds. In the presence of linear 1,3-dicarbonyl compound construction of carbon–carbon bonds was happened which is a fundamental task in organic synthesis [9,10]. On the other hand, condensation of cyclic 1,3-dicarbonyl compound with alcohols produce β-keto enol ethers which have been widely used as key intermediates in organic

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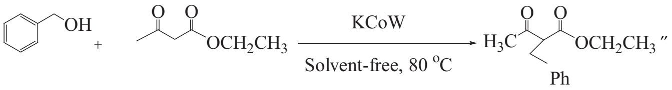
Table 1
Optimization of the conditions.[a].



Entry	Catalyst (g)	Time (min)	Yield (%)[b]
1	–	60	5
2	KCoW (0.04)	15	10
3	KCoW (0.06)	15	54
4	KCoW (0.08)	15	95
5	KCoW (0.1)	12	96
6	KCoW (0.08)[c]	60	29

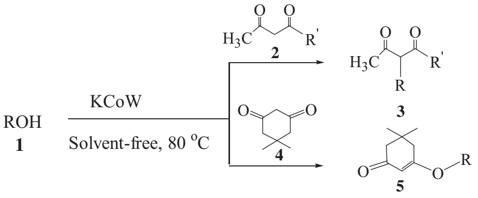
[a] Reaction conditions: benzyl alcohol (1 mmol), ethylacetoacetate (1 mmol), 80 °C, solvent-free conditions.
[b] Isolated yield.
[c] Reaction proceed at room temperature.

synthesis [11,12]. As a starting point for optimization of the reaction conditions, the reaction of benzyl alcohol and ethylacetoacetate was chosen as a model reaction (Table 1). The substrates did not react in the absence of the catalyst (entry 1). To investigate the effect of the catalyst loading, the model reaction was carried out in the presence of different amounts of the catalyst. The best result was obtained in the presence of 0.08 g of KCoW, and the use of higher amounts of the catalyst, were slightly decreased the reaction time (entries 2–5). Only 29% yield of the corresponding product was obtained in the presence of KCoW at room temperature even after 60 min (entry 6).

Encouraged by these results, we turned our attention to various cyclic and linear 1,3-dicarbonyl compounds and benzylic alcohols (Table 2). Reaction of the linear 1,3-dicarbonyls such as acetylacetone with different types of alcohols proceeded smoothly providing 89–96% yields (entries 1–13). Employing 5,5-dimethylcyclohexane-1,3-dione (dimedone), as a cyclic 1,3-dicarbonyl using the same reaction conditions dose not produced corresponding 2-benzylic-1,3-dicarbonyl compound and an unknown compound was generated as main product (entry 15). This compound was isolated by column chromatography and characterized by FTIR, NMR, and CHN techniques. The results indicated that the unknown compound is the corresponding β-keto enol ethers (**5a**). Due to the wide range applications of β-keto enol ethers as synthons in several key intermediate compounds, various alcohols were treated with dimedone as a cyclic 1,3-dicarbonyl compound. Towards these studies, effect of the amount of the catalyst and reaction temperature was investigated (entries 16–20). Only 10% of corresponding product was obtained at room temperature (entry 20). The present conversion with primary alcohols proceeded rapidly to form the products in high to excellent yields. *tert*-Butyl alcohol as substrate afforded trace amount of corresponding product after 1.5 h (entry 25). More amount of the catalyst (0.2 g) was not improved the yield of this reaction. It should be mentioned that no acetal adducts were detected, even in the case of linear 1,3-diketones for which it has been reported [12]. This protocol was then applied to secondary, vinyl or substituted benzyl alcohols and benzhydril which are structurally different. Reactions with these type alcohols obtained lower yield. In order to prove catalytic activity of KCoW *via* electron-transfer mechanism, a radical scavenger (acrylonitrile) was added to the model reaction after 10 min (when about 50% of the corresponding product was obtained). After continuation of the reaction until 25 min, yield of the product was 52% and it seems that the reaction was stopped by addition of radical scavenger. More investigation about the mechanism of the catalyst is under investigation in our laboratory.

To check that is this catalyst completely heterogeneous or not, the model reaction (Scheme 1) was carried out for 15 min, until yield of the product was 60%. Then, the reaction was stopped, catalyst was recovered according to the procedure and separated by centrifugation and the filtrate was stirred again, no improvement was observed even after 1 h. This observation confirmed that the reaction was catalyzed heterogeneously. In addition, the content of W into filtrates was evaluated quantitatively by inductively coupled plasma atomic emission spectroscopy (ICP-AES), which showed just trace amount of the W. The stability of the catalyst has been studied by running the reaction successively with the same catalyst in the same reaction. Fig. 1 shows the results of this study. It is interesting to note that the catalyst could be used several times in one reaction with a little change in its percentage of the yield. Possible mechanisms for catalytic addition of different diketones to alcohols are proposed (Scheme 1, pathways 1 and 2). By action of KCoW the alcohol was protonated to generate a stable carbocation after dehydration. This carbocation could

Table 2
Benzylation of different 1,3-dicarbonyl compounds catalyzed by KCoW.



1a: R= $PhCH_2$
1b: R= $(Ph)_2CH$
1c: R= 4-Cl-$PhCH_2$
1d: R= 2-MeO-$PhCH_2$
1e: R= $(Ph)(CH_3)CH$
1f: R= 4-MeO-$PhCH_2$
1g: R= $CH_3(CH_2)_3$
1h: R=CH_3CH_2

1i: R= $CH_3(CH_2)_2$
1j: R= $CH_3(CH_2)_5$
1k: R= $(CH_3)_2CH$
1l: R= C_6H_{11}
1m: R= $(CH_3)_3CH$
1n: R= 4-NO_2-$PhCH_2$
1o: R= 2-NO_2-$PhCH_2$
1p: R= Cinamyl

2a: R'= OCH_2CH_3
2b: R'= OCH_3
2c: R'= CH_3

Entry	Alcohol	Diketone	Product	Catalyst (g)	Time (min)	Yield (%)[a]
1	**1a**	**2a**	**3aa**	0.08	15	95
2	**1b**	**2c**	**3bc**	0.08	20	89
3	**1b**	**2b**	**3bb**	0.08	15	96
4	**1b**	**2a**	**3ba**	0.08	15	91
5	**1a**	**2c**	**3ac**	0.08	20	92
6	**1a**	**2b**	**3ab**	0.08	15	95
7	**1c**	**2a**	**3ca**	0.08	20	93
8	**1d**	**2c**	**3dc**	0.08	15	98
9	**1d**	**2b**	**3db**	0.08	15	90
10	**1d**	**2a**	**3da**	0.08	15	95
11	**1e**	**2c**	**3ec**	0.08	15	90
12	**1f**	**2c**	**3fc**	0.08	15	94
13	**1g**	**2c**	**3gc**	0.08	25	15[b]
14	**1p**	**2c**	**3pc**	0.08	15	95
11	**1a**	**4**	**5a**	0.08	30	89
12	**1h**	**4**	**5d**	0.04	25 (45)	45 (61)
13	**1h**	**4**	**5d**	0.06	25 (35)	60 (75)
14	**1h**	**4**	**5d**	0.08	25	95
15	**1h**	**4**	**5d**	0.1	25	95
16	**1h**	**4**	**5d**	0.08	25	10[c]
17	**1i**	**4**	**5e**	0.08	25	96
18	**1j**	**4**	**5f**	0.08	30	94
19	**1k**	**4**	**5g**	0.08	70	75
20	**1l**	**4**	**5h**	0.08	75	81
21	**1m**	**4**	**5i**	0.08	90	Trace[b]
22	**1a**	**4**	**5a**	0.08	30	89
23	**1d**	**4**	**5j**	0.08	35	84
24	**1n**	**4**	**5k**	0.08	45	91
25	**1o**	**4**	**5l**	0.08	70	82
26	**1p**	**4**	**5m**	0.08	35	86

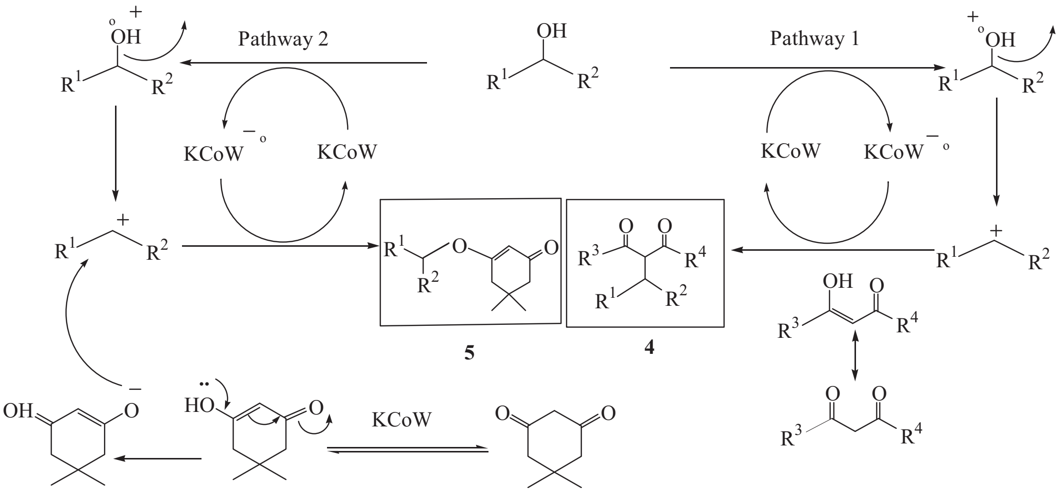
[a] Isolated yield.

[b] More amount of the catalyst (0.2 g) was not improved the yield of this reaction.

[c] Reaction proceeded at room temperature.

quickly combine with the employed 1,3-dicarbonyl compound to produce, after the release of H^+, the final alkylated product. Also, due to the resonance of oxygen with adjacent π-bonding electrons, cyclic 1,3-dicarbonyl compound as a nucleophile combined with the stable carbocation to produce β-keto enol ethers.

KCoW catalyst were prepared and purified according to literature procedures [13]. For the benzylation of 1,3-dicarbonyl compound, the catalyst (0.08 g), was added to a mixture of alcohol (1.0 mmol) and 1,3-dicarbonyl compound (1.0 mmol) at 80 °C. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was diluted with acetonitrile, and then the catalyst was removed by centrifugation. Catalyst was collected and treated with 1,2-dichloroethane for removing coke followed by vacuum drying and calcinations at 150 °C, 1 h for reusing. The filtrate was concentrated and the product was purified by column chromatography on silica-gel using EtOAc/hexane (1:3) as eluent. For the synthesis of β-keto enol ethers, a mixture of dimedone (1.0 mmol) and alcohol (4 mL) was stirred well in the presence of the catalyst (0.08 g) at 80 °C. After complete consumption of the starting materials as indicated by TLC, the reaction was filtered. The excess alcohol in the filtrate was removed by rotary



Scheme 1. Proposed mechanisms for catalytic addition of different diketones to alcohols.

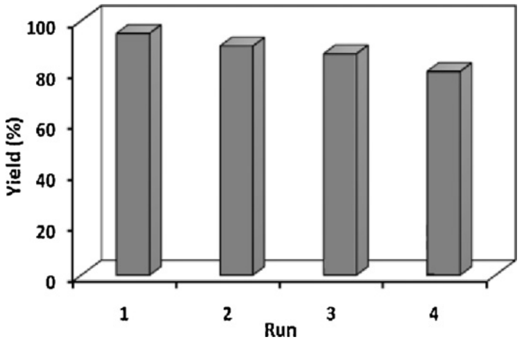


Fig. 1. Reusability of the KCoW in the reaction of benzyl alcohol (1 mmol), ethylacetoacetate (1 mmol), catalyst (0.08 g), 80 °C under solvent-free conditions after 30 min.

evaporation and the crude purified by column chromatography over silica-gel (ethyl acetate/hexane, 1:4). All the products were identified by comparing of their spectral data with those of the authentic samples [14–16].

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