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Heteropoly acid-catalyzed highly efficient alkylation of 1,3-dicarbonyl compounds with benzylic and propargylic alcohols

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ABSTRACT

Various 1,3-dicarbonyl compounds reacted readily with benzylic and propargylic alcohols in the presence of 10 mol % of phosphomolybdic acid supported on silica gel (PMA/SiO_2) under mild reaction conditions to produce 2-benzylic- and 2-propargylic-1,3-dicarbonyl compounds in excellent yields and with high selectivity.

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The alkylation of 1,3-dicarbonyl compounds is a useful transformation involving C–C bond formation. In principle, direct nucleophilic substitution of the hydroxy group in alcohols with nucleophiles generally requires preactivation of the alcohol because of its poor leaving ability.[1] Consequently, hydroxyl groups are generally transformed into the corresponding halides, carboxylates, carbonates, phosphonates or related compounds.[2] However, such processes inevitably produce stoichiometric amounts of salt waste, and also substitution with halides requires a stoichiometric amount of base which limits their use in scale-up. In most cases, either a high reaction temperature or a promoter is required to enhance the leaving ability of the hydroxyl group. Subsequently, transition-metal based reagents such as palladium in the presence of a base or acid and stoichiometric amounts of cobalt salts have been reported for the direct nucleophilic substitution of unmodified alcohols.[3] Most of these methods worked well only with allylic alcohols but not with benzylic alcohols. Recently, acid catalysts such as $BF_3{\cdot}OEt_2$, $InCl_3$, $Bi(OTf)_3$, $Yb(OTf)_3$, $FeCl_3$ and H-montmorillonite have been employed to perform nucleophilic substitution of benzylic alcohols with active methylene compounds.[4,5] However, the use of high temperatures, extended reaction times and harsh conditions in many of the above-mentioned methods limit their practical utility in large scale synthesis. Moreover, little has been explored on nucleophilic substitution of propargylic alcohols with 1,3-dicarbonyls.[6] Therefore, the direct catalytic substitution of alcohols with 1,3-dicarbonyls using an efficient, cost-effective and recyclable catalyst is highly desirable.

Recently, the use of heteropoly acids, HPAs, as environmentally friendly and economically viable solid acids, has gained increasing attention owing to their ease of handling and high catalytic activities and reactivities.[7] These compounds possess unique properties, such as well-defined structure, Bronsted acidity, the possibility to modify their acid–base and redox properties by changing their chemical composition (substituted HPAs), ability to accept and release electrons, high proton mobility, etc.[8] In view of green chemistry, the substitution of harmful liquid acids by reusable solid HPAs as catalysts in organic synthesis is a promising application of these acids.[9] Among them, phosphomolybdic acid (PMA, $H_3PMo_{12}O_{40}$) is one of the less expensive and commercially available catalysts.[10] However, there have been no reports on the use of phosphomolybdic acid for the direct alkylation of 1,3-dicarbonyl compounds with benzylic and propargylic alcohols.

In continuation of our efforts to explore the synthetic utility of phosphomolybdic acid supported on silica gel (PMA/SiO_2),[11] we herein report a direct and efficient protocol for the alkylation of 1,3-dicarbonyl compounds with benzylic and propargylic alcohols. Initially, we attempted the alkylation of acetyl acetone (**1**) with diphenylmethanol (**2**) in the presence of 10 mol% of PMA/SiO_2. The reaction went to completion at room temperature within 2.0 h to give product **3a** in 92% yield (Scheme 1).

This interesting catalytic activity of PMA/SiO_2 provided the incentive for further study of reactions with other active methylene compounds. Interestingly, 1,3-dicarbonyl compounds such

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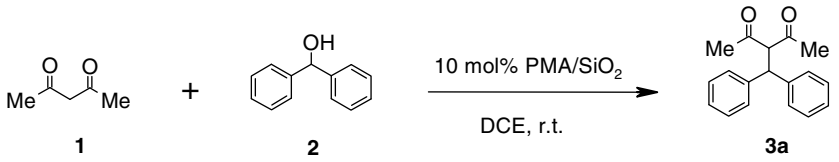

Scheme 1.

Table 1
PMA/SiO_2-catalyzed alkylation of 1,3-diketones with benzylic alcohols

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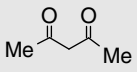
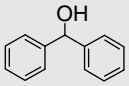
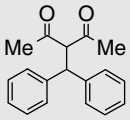
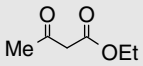
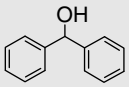
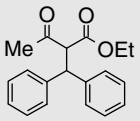
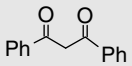
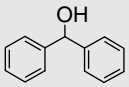
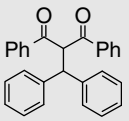
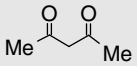
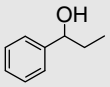
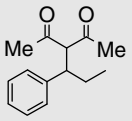
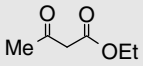
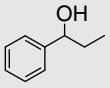
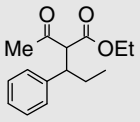
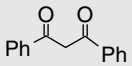
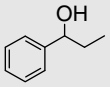
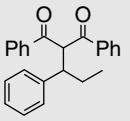
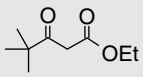
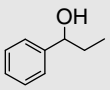
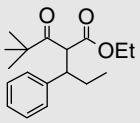
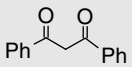
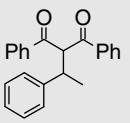
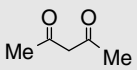
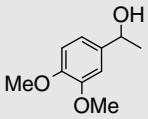
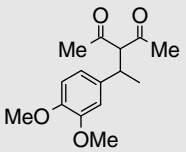
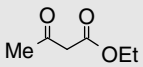
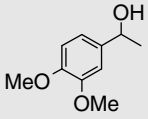
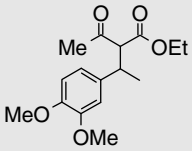
a				2.0	92
b				2.5	90
c				2.0	90
d				1.5	88
e				3.0	65
f				2.5	88
g				2.0	75
h				2.5	88
i				2.0	93
j				2.5	82

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