

ORGANIC CHEMISTRY | RESEARCH ARTICLE

K₂CO₃/Al₂O₃: An efficient and recyclable catalyst under solvent free conditions for the reaction of electron-deficient nitro-olefins with 1,3-dicarbonyl compounds

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K_2CO_3/Al_2O_3 : An efficient and recyclable catalyst under solvent free conditions for the reaction of electron-deficient nitro-olefins with 1,3-dicarbonyl compounds

Abdullah M.A. Shumaila^{1*}

Abstract: K_2CO_3/Al_2O_3 (KCA) is an efficient heterogeneous catalyst for the Michael addition reaction of 1,3-dicarbonyl compounds to nitro olefin under thermal solvent-free conditions. The results showed that the catalyst has high activity and the desired products were obtained in high yields. Furthermore, the products could be separated simply from the catalyst, and the catalyst could be recycled and reused with only slight reduction in its catalytic activity.

Subjects: Chemistry; Organic Chemistry; Inorganic Chemistry

Keywords: KCA; Michael donors and acceptors; recyclable catalysis; solvent-free

1. Introduction

Among the C–C bond-forming reactions, the Michael addition of various nucleophiles to highly electron deficient nitro olefins has received great attention (1). It provides a convenient access to valuable synthones and building blocks, which may lead to a variety of important biologically active compounds and pharmaceuticals, due to the ease of transformation of the nitro group (2, 3).

The conjugate addition of enolates to activated olefins remains an active field of research. Indeed, the conjugate addition of carbon-based nucleophiles to electron deficient nitro olefins is one of the



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PUBLIC INTEREST STATEMENT

Michael reaction of nitro-olefins represents a convenient access to nitroalkanes that are versatile intermediates in organic synthesis. The nitro functionality can be easily transformed into amine, nitrile oxide, ketone or carboxylic acid, hydrogen, etc., providing a wide range of synthetically interesting compounds. Therefore, in this paper, a simple and efficient method for the synthesis of these compounds by the conjugate addition reaction of 1,3-dicarbonyl compounds to nitro-olefins using K_2CO_3/Al_2O_3 as catalyst has been reported. The method was fast and the desired products were obtained within a few minutes in high yields under solvent-free conditions. Other advantages of this protocol include inexpensive and easily obtained catalyst, simple work-up, and the recyclability and reusability of the catalyst.

classical methods for C–C bond construction. Direct Michael addition and Michael-type conjugate reactions are among the most simple, efficient and atom-economical ways to achieve this transformation. These reactions are typically performed with stoichiometric amounts of inorganic bases such as alkali metal alkoxides (4). Several undesirable side reactions can be caused by these strongly basic catalysts, including rearrangements, secondary condensations, isomerizations, polymerizations, bis additions, retrogressions, and *trans*-esterifications. In the Literature survey, some of improved procedures have been reported using $\text{LiClO}_4/\text{Et}_3\text{N}$ (5), bis(2,4-pentanedionato)nickel (II) (4b), $\text{NaOH}/\text{BImPF}_6$ system (6), transition metal complexes of BINOL-derived salens (7), a quaternary ammonium salt (8), L-proline (9), cinchona alkaloids (10), imidazolidine (11), DBU (12), TBD (13a) and bifunctional thiourea (14). On the other side, excellent enantioselective Michael reactions have been developed using catalysts, like bis(oxazoline)- $\text{Mg}(\text{OTf})_2$ (1c), demethylquinine salts in water (15), and Nickel(II)-diamine complexes (16). However, some of these methods suffer from the drawback of not having use of green chemistry and have been associated with several shortcomings such as long reaction times, expensive reagents, low product yields and difficulty in recovery and reusability of the catalysts. Due to these problems, development of an efficient and versatile method using heterogeneous and reusable catalysts is still in demand.

In recent years, heterogeneous catalysts have gained great importance in different areas of organic synthesis due to their economic and environmental compatibility combined with the good yield and selectivity that can be achieved (17). In addition, the activity and selectivity of a reagent dispersed on the surface of a support are improved as the effective surface area of the reagent is increased significantly, and hence they are expected to perform more effectively than the individual reagents (18). Among the various supported catalysts, particularly, alumina and silica supported reagents have advantages of low cost, ease of preparation, and catalyst recycling (19).

On the other hand, the current considerable interest has been devoted to finding new methodologies for the synthesis of organic compounds in solvent-free conditions (19c, 20). The toxicity and volatile nature of many organic solvents have posed a serious threat to the environment. Thus, design of solvent-free catalytic reaction has received tremendous attention in recent times in the area of green synthesis (21).

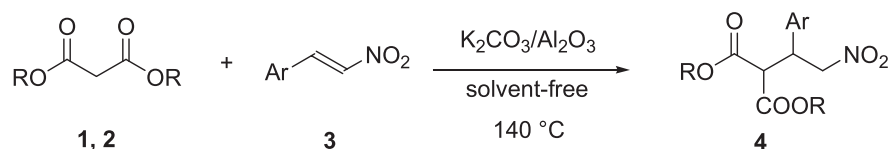
Considering the above facts and due to our interest in the solid catalysts and in solid-supported synthesis for organic reactions (22), we report herein the investigation of $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$ (KCA) as an efficient, low cost and heterogeneous reusable catalyst for the reaction of electron-deficient nitroolefins with 1,3-dicarbonyl compounds under solvent-free conditions.

2. Result and discussion

In the present work and as a reliable starting point, diethyl malonate **1** (1.1 mmol) was used as the Michael donor and nitro olefin **3a** (1 mmol) as Michael acceptors. After that, the performance of $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$ (KCA) (23) as a solid base supported catalyst along with its ability as a reusable catalyst was evaluated for this conjugate addition reaction, which chosen as model to afford the product **4a** (Ar = phenyl, R = Et, Scheme 1) under solvent-free conditions. A summary of obtained results is provided in Table 1.

Initially, to establish the optimal conditions, a set of experiments varying the amount of the catalyst and temperature were carried out. As can be seen from Table 1, the efficiency of the reaction is affected mainly by the amount of the catalyst (KCA). Low yield of the product **4a** was produced in the absence of the catalyst at 140°C (entry 1) indicating that the catalyst KCA is necessary for a high yield. Increasing the amount of the catalyst increased the yield of the product **4a**. The best result was obtained when the reaction was run at 140°C in the presence of 0.15 g as optimal amount of KCA under solvent-free conditions (entry 10, 98%). An increase in the reaction temperature and amount of the catalyst did not improve the yields significantly. Also the model reaction was tested in the presence of only K_2CO_3 at 140°C under solvent-free conditions; however, this reagent was not efficient separately (entry 12). Indicating that, it is necessary to support K_2CO_3 on the alumina (Al_2O_3).

Scheme 1. Synthesis of various Michael adducts 4a-h using KCA as a catalyst.



1. R = Et, **4a.** Ar = phenyl, R = Et; **4b.** Ar = 3,4-methylenedioxyphenyl, R = Et; **4c.** Ar = 4-methoxyphenyl, R = Et; **4d.** 2-furyl, R = Et; **4e.** Ar = 2-thienyl, R = Et; **2.** R = Me; **4f.** Ar = phenyl, R = Me; **4g.** Ar = 4-methoxyphenyl, R = Me; **4h.** 2-furyl, R = Me.

Table 1. Synthesis of compound 4a using KCA as catalyst

Entry	Catalyst (g)	T (°C)	Time (min)	Yield (%) ^a
1	None	140	60	19
2	KCA (0.05)	80	15	52
3	KCA (0.05)	110	15	61
4	KCA (0.05)	140	15	64
5	KCA (0.10)	80	15	68
6	KCA (0.10)	110	15	71
7	KCA (0.10)	140	15	75
8	KCA (0.15)	80	20	79
9	KCA (0.15)	110	15	83
10	KCA (0.15)	140	8	98, 97, 96, 95, 95 ^b
11	KCA (0.20)	140	10	96
12	K ₂ CO ₃ (0.50)	140	60	62

^aIsolated yields.

^bThe same catalyst was used for each of five runs.

Subsequently, we examined the recycling performance of KCA in the model reaction. Entry 10 described the yields of five consecutive additions leading to **4a**. In these experiments, the product was isolated by filtration and washing the solid residues with ethanol. Thus, the remaining catalyst, which always works the same, begins reloading with fresh reagents for further runs. We found that the catalyst could be used at least five times with only a slight reduction in activity, demonstrating the efficiency of K₂CO₃/Al₂O₃ (KCA) as a catalyst in Michael addition reactions. Therefore, the solid KCA is a truly heterogeneous efficient catalyst for this conjugate addition.

The previously mentioned results indicated that K₂CO₃/Al₂O₃ reaction at 140°C under solvent-free condition furnished maximum yield of the conjugate addition reactions in the short time. Furthermore, KCA is reusable and environmentally benign, presenting fewer disposal problems, which can be a good alternative.

After achieving the optimized reaction conditions, we examined the generality of the catalytic efficiency of KCA using other nitro olefins having different substituents. In all cases the reactions were complete in few minutes affording products in high yields. The results are summarized in Table 2. Instead of diethyl malonate, dimethyl malonate has been used with similar success to provide the corresponding products (**4f-h**, Table 2). The structures of all products were confirmed by ¹H NMR and ¹³C NMR spectroscopy and compared with those reported in the literature (13, 14).

Table 2. Scope of the malonate Michael addition with nitroalkenes 3a–e

Reaction scheme: $\text{RO-CO-CH}_2\text{-CO-OR} + \text{Ar-CH=CH-NO}_2 \xrightarrow[\text{solvent-free}]{\text{KCA, 140 }^\circ\text{C}}$ $\text{RO-CO-CH(Ar)-CH(COOR)-NO}_2$

Entry	R	Ar	Product 4	Time (min)	Yield (%) ^a
1	Et (1)	phenyl (3a)	4a	8	98
2	Et (1)	3,4-methylenedioxyphenyl (3b)	4b	13	92
3	Et (1)	4-methoxyphenyl (3c)	4c	13	93
4	Et (1)	2-furyl (3d)	4d	12	94
5	Et (1)	2-thienyl (3e)	4e	12	90
6	Me (2)	phenyl (3a)	4f	9	95
7	Me (2)	4-methoxyphenyl (3c)	4 g	13	92
8	Me (2)	2-furyl (3e)	4 h	11	91

^aIsolated yields.

3. Conclusion

In summary, we have established successful conjugate addition reaction of 1,3-dicarbonyl compounds to nitro olefin in the presence of a catalytic amount of $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$ as an efficient, reusable, and green heterogeneous catalyst under solvent-free conditions. Moreover, the method offers several advantages such as ease of workup, high yields, stability and recyclability and reusability of the catalyst. The catalyst can be used at least five times without substantial reduction in its catalytic activity. Hence, we believe that this method will find wide application in organic synthesis as well as industry.

4. Experimental

To a mixture of dialkyl malonate (1.1 mmol) and nitro olefin (1 mmol) in a round-bottom flask connected to a reflux condenser was added $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$ (0.15 g), and the resulting mixture was stirred in an oil-bath at 140 °C for an appropriate duration of time (8–13 min). The reaction was monitored by thin-layer chromatography (TLC). Upon completion, the reaction mixture was cooled to room temperature, hot ethanol (20 ml) was added and filtered to remove the catalyst. Again the catalyst was washed with 10 ml of absolute ethanol (hot). The remaining catalyst was reloaded with fresh reagents for further runs. The solvent of combined filtrate was evaporated by rotary evaporator, and the crude product was recrystallized from ethyl acetate/n-hexane (1:3) or ethanol.

4.1. Selected data

Compound **4a** was obtained in 98% yield. MP 43–45 °C; ν_{max} 1735 (b, 2 × CO), 1556, 1375 (NO_2); ^1H NMR (300 MHz, CDCl_3): δ 1.03 (t, $J = 7.0$ Hz, 3H, OCH_2CH_3), 1.25 (t, $J = 7.3$ Hz, 3H, OCH_2CH_3), 3.82 (d, $J = 9.4$ Hz, 1H, $(\text{CO})_2\text{-CH}$), 3.99 (q, $J = 7.3$ Hz, 2H, OCH_2CH_3), 4.18–4.29 (m, 3H, $[\text{OCH}_2\text{CH}_3, \text{Ar-CH}]$), 4.81–4.98 (m, 2H, $\text{CH}_2\text{-NO}_2$), 7.21–7.35 (m, 5H, ArH); ^{13}C NMR (75 MHz, CDCl_3): δ 13.6, 13.8, 42.8, 54.9, 61.8, 62.0, 77.5, 127.9, 128.2, 128.8, 136.1, 166.7, 167.3; MS: m/z 263 $[\text{M} - (\text{NO}_2)]^+$, 189 (100%).

Compound **4f** was obtained in 90% yield. MP 42–44 °C; ν_{max} 1735, 1728 (2 × CO), 1556, 1373 (NO_2); ^1H NMR (300 MHz, CDCl_3): δ 3.55 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 3.86 (d, $J = 9.0$ Hz, 1H, $(\text{CO})_2\text{-CH}$), 4.22–4.27 (m, 1H, Ar-CH), 4.81–4.96 (m, 2H, $\text{CH}_2\text{-NO}_2$), 7.21–7.35 (m, 5H, ArH); ^{13}C NMR (75 MHz, CDCl_3): δ 42.8, 52.7, 52.9, 54.6, 77.4, 127.8, 128.3, 128.9, 136.0, 167.2, 167.8; MS: m/z 235 $[\text{M} - (\text{NO}_2)]^+$, 175 (100%).

Supporting information

Full experimental details and ^1H and ^{13}C spectra are available. This material can be found via the "Supplemental Content" section of this article's Web page.

Supplementary material

Supplementary material for this article can be accessed here <https://doi.org/10.1080/23312009.2018.1455346>.

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Competing interests

The author declare no competing interest.

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