A Facile, Catalytic and Environmentally Benign Method for Esterification of Carboxylic Acids and Transesterification of Carboxylic Esters with Nearly Equimolar Amounts of Alcohols

D. Subhas Bose,* Apuri Satyender, A. P. Rudra Das, Hari Babu Mereyala

Organic Chemistry Division III, Fine Chemical Laboratory, Indian Institute of Chemical Technology, Habshiguda, Hyderabad – 500 007, India

Fax +91(40)27160387; E-mail: bose_iict@yahoo.co.in; dsb@iict.res.in

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Abstract: A practical and green chemical process for the esterification of carboxylic acids with alcohols and transesterification of carboxylic esters in good to excellent yields by using $K_5COW_{12}O_{14}$ · $3H_2O$ (0.1 mol%) as catalyst is reported. The catalyst exhibited remarkable reusable activity.

Key words: esterification, transesterification, alcohols, carboxylic acids, reusable

Esterifications and transesterifications are widely recognized as one of the most important reactions in organic synthesis. The ester moiety represents one of the most ubiquitous functional groups in chemistry, playing a paramount role in biology and serving both as key intermediate and/or protecting group in organic transformations. Besides its utility in the laboratory, this reaction is significant in various industrial processes, such as the production of fatty acids, paints, polyesters, etc. Since esterification is an equilibrium process, carrying out the reaction with a large excess of one of the two reactants usually performs the full conversion into the products. Recently, the growing interest towards green chemistry led to the development of a new generation of protocols which aimed at a 1:1 stoichiometry between the acid and the alcohol under mild and almost neutral conditions. A number of useful and reliable esterification methods catalyzed by a variety of acids, ion exchange resins, zeolites, etc., have been reported in the literature.¹⁻¹¹ Environmental considerations limit the applicability of many, otherwise useful catalysts commercially. There are not many reagents available for commercial applications that can accomplish both esterification and transesterification reactions under mild conditions. Transesterifications are catalyzed by alkali metal hydroxides and alkoxides in appropriate alcohols and also by DMAP, DBU, PTSA, tin, calcium or titanium compounds.12

From a recent atom-economical standpoint, the use of nearly equimolar amounts of carboxylic acids (or carboxylic esters) and alcohols is strongly required. Mukaiyama and Shiina reported¹³ such direct esterifications mediated by $TiCl_2(ClO_4)_2$ and $TiCl(OTf)_3$ reagents; however, they

necessitated more than equimolar amounts of anhydride and silyl dehydrating additives, respectively. The employment of non-sophisticated and recyclable catalyst undoubtedly represents an additional important goal.

In the course of our studies on the use of heterogeneous catalysis in fine organic chemistry, we developed a method, which allows the practical route for esterification, transesterification and simultaneous esterification and transesterification reactions by using inexpensive and reusable K_5 Co $W_{12}O_{40}$ ·3 H_2O (0.1 mol%) catalyst¹⁴ in a highly efficient manner. To our knowledge, however, the generality and applicability of potassium dodecatangestocobaltate trihydrate (PDTC) to accomplish these reactions have not appeared so far. We initially investigated the catalytic activity of PDTC, which promotes the esterification reaction between equimolar amounts of 3-phenylpropionic acid and butan-1-ol in toluene, carried out under azeotropic reflux conditions with removal of water using a Dean–Stark apparatus for five hours (Table 1, entry 3). We found that under the best reaction conditions, namely in the presence of 0.1 mol% of PDTC full conversion into the ester occurred in five hours. PDTC in excess of five equivalents did not help to increase the yield to any greater extent (Table 1, entry 5). The progress of reaction was monitored either by TLC or GC. The reaction mixture was filtered to separate the catalyst, and the filtrate was evaporated in vacuo to furnish the product. Moreover, the recovered catalyst from the reaction mixture washed with solvent, and could be reused after thermal activation. The reactivated catalyst was reused without an appreciable loss of its catalytic activity (Table 2, entry 1). For example, the catalyst was reused for the esterification of phenylacetic acid with butan-1-ol more than three times with 93%, 91%, and 89% yields, respectively.

To explore the generality and scope of esterification process, diverse acids such as saturated, unsaturated, hydroxy and dicarboxylic acids were esterified with a variety of alcohols. The reactions proceeded in high yields at relatively low temperatures (85–100 °C) and the results are summarized in Table 2. The esterification process worked well with primary, secondary, tertiary, benzylic and homoallylic alcohols (Table 2, entries 1–20) with the reactivity of the alcohols decreasing in the order of primary > secondary > tertiary and neither isomerization of the substrate (entries 5 and 9) nor racemization (entry 7) were ob-

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Table 1 Optimization in the Esterification of 3-Phenylpropionic Acid with Butan-1-ol

| Ph | + | Me(CH ₂) ₃ OH | toluene | Ph COO(CH ₂) ₃ Me | | |
|-------|---|--|----------------------------------|--|----------|-----------|
| Entry | | Catalyst (mc | ol%) | | Time (h) | Yield (%) |
| 1 | | K ₅ CoW ₁₂ O ₄₀ | $_{0}$ ·3H ₂ O (0.01) | | 5 | 25 |
| 2 | | K ₅ CoW ₁₂ O ₄₀ | $_{0}$ ·3H ₂ O (0.05) | | 7 | 70 |
| 3 | | K ₅ CoW ₁₂ O ₄₀ | $_{0}$ ·3H ₂ O (0.1) | | 5 | 95 |
| 4 | | K ₅ CoW ₁₂ O ₄₀ | $_{0}$ ·3H ₂ O (0.1), | molecular sieves | 8 | 90 |
| 5 | | K ₅ CoW ₁₂ O ₄₀ | $_{0}$ ·3H ₂ O (0.15) | | 10 | 86 |

| R | OH + R ¹ -OH | K ₅ CoW ₁₂ O ₄₀ ·3H ₂ O | | | | |
|-------|--|---|-----------|----------|---|------------------------|
| Entry | RCO ₂ H | R ¹ OH | Temp (°C) | Time (h) | Product | Yield (%) ^b |
| 1 | PhCH ₂ CO ₂ H | Me(CH ₂) ₃ OH | 85 | 5 | PhCH ₂ CO ₂ (CH ₂) ₃ Me | 93, 91, 89° |
| 2 | PhCH ₂ CO ₂ H | PhCH ₂ OH | 85 | 7 | PhCH ₂ CO ₂ CH ₂ Ph | 88 |
| 3 | PhCH ₂ CO ₂ H | Me(CH ₂) ₇ OH | 85 | 5 | PhCH ₂ CO ₂ (CH ₂) ₇ Me | 93 |
| 4 | PhCH ₂ CO ₂ H | TBDMSO(CH ₂) ₄ OH | 85 | 4 | PhCH ₂ CO ₂ (CH ₂) ₄ OTBDMS | 92 |
| 5 | Ph(CH ₂) ₂ CO ₂ H | CH ₂ =CHCH ₂ OH | 85 | 4 | Ph(CH ₂) ₂ CO ₂ CH ₂ CH=CH ₂ | 90 |
| 6 | Ph(CH ₂) ₂ CO ₂ H | CH ₃ (CH ₂) ₇ OH | 85 | 6 | Ph(CH ₂) ₂ CO ₂ (CH ₂) ₇ Me | 93 |
| 7 | Ph(CH ₂) ₂ CO ₂ H | OH | 85 | 25 | OCCH ₂ CH ₂ Ph | 87, 72 |
| 8 | c-C ₆ H ₁₁ CO ₂ H | MeCH(OH)(CH ₂) ₅ Me | 100 | 25 | $c-C_6H_{11}CO_2CH(Me)(CH_2)_5Me$ | 65 |
| 9 | Ph(CH ₂) ₂ CO ₂ H | NO ₂ CH ₂ CH ₂ OH | 85 | 6 | $Ph(CH_2)_2CO_2CH_2CH_2NO_2$ | 85 |
| 10 | Ph(CH ₂) ₂ CO ₂ H | (Z)-EtCH=CH(CH ₂) ₂ OH | 85 | 5 | (Z)-Ph(CH ₂) ₂ CO ₂ (CH ₂) ₂ CH=CHEt | 89 |
| 11 | 4-MeC ₆ H ₄ CO ₂ H | MeCH(Me)CH ₂ CH ₂ OH | 85 | 6 | 4-MeC ₆ H ₄ CO ₂ (CH ₂) ₂ CH(Me)Me | 85 |
| 12 | PhCH=CHCO ₂ H | Me(CH ₂) ₃ OH | 85 | 5 | PhCH=CHCO ₂ (CH ₂) ₃ Me | 89 |
| 13 | CH ₂ =CH(CH ₂) ₈ CO ₂ H | EtOH | 85 | 5 | CH ₂ =CH(CH ₂) ₈ CO ₂ Et | 90 |
| 14 | CH ₂ =CH(CH ₂) ₈ CO ₂ H | Me(CH ₂) ₈ OH | 85 | 5 | CH ₂ =CH(CH ₂) ₈ CO ₂ (CH ₂) ₈ Me | 91 |
| 15 | $HO_2C(CH_2)_4CO_2H$ | MeOH | 85 | 8 | MeO ₂ C(CH ₂) ₄ CO ₂ Me | 82 |
| 16 | $HO_2C(CH_2)_4CO_2H$ | Me(CH ₂) ₃ OH | 85 | 6 | $Me(CH_2)_3O_2C(CH_2)_4CO_2(CH_2)_3Me$ | 87 |
| 17 | PhCH=CHCO ₂ H | t-BuOH | 85 | 8 | PhCH=CHCO ₂ Bu- <i>t</i> | 84 |
| 18 | HO ₂ C(CH ₂) ₈ CO ₂ H | t-BuOH | 85 | 9 | t-BuO ₂ C(CH ₂) ₈ CO ₂ Bu- t | 80 |
| 19 | 2-OHC ₆ H ₄ CO ₂ H | <i>i</i> -PrOH | 85 | 6 | 2-OHC ₆ H ₄ CO ₂ Pr- <i>i</i> | 88 |
| 20 | HO ₂ CCH ₂ CO ₂ H | <i>i</i> -PrOH | 85 | 8 | <i>i</i> -PrO ₂ CCH ₂ CO ₂ Pr- <i>i</i> | 78 |

^a Reaction conditions: 1.0 mmol alcohol, 1.0 mmol carboxylic acid, 0.1 mol% catalyst.

^b The yields reported refer to isolated products.

^c Catalyst was reused at least three times.

served. The yields of the products also showed a trend in the same order as that of the reactivity.

It is well known that the reactivity of alcohols and carboxylic acids towards esterification primarily depends on the steric hindrance of both the reactants. We found that acids bearing at the α position a bulky cyclohexyl (entry 8) group gave the desired ester, although a higher temperature or a higher catalyst loading was required to obtain good yields. Nevertheless, the reactions were carried at 100 °C at the most, since at higher temperatures some decomposition of the product occurred. Very good results were obtained in the case of low reactive carboxylic acids (entries 11 and 12), and wax esters, i.e. esters of long chain carboxylic acids with long chain alcohols, which are generally prepared via acyl chlorides, are also easily prepared by this method. Esters of tertiary alcohols that are otherwise difficult to prepare are obtained in moderate yields (entries 17,18) but required longer reaction times and increased amounts of catalyst since the dehydration process largely prevailed over the condensation.

The reaction is highly chemoselective. In fact, other functionalities present in the carboxylic acid or in the alcohol, such as a carbonyl, a cyano and a nitro group, a C-C double bond or a bromide were unaffected under the adopted reaction conditions. The compatibility of some typical protecting groups with the reaction conditions was also evaluated. Other functional groups present in the alcohol, such as, benzyl and o-silyl were almost completely unaffected (entries 2 and 4). Butyl lactate, a valuable intermediate for the production of butyl acrylate, is prepared in an efficient manner by esterification of commercial lactic acid (88%) with butan-1-ol even in the presence of high amounts of water (12%) in the lactic acid. It is well known that esterification reactions are highly sensitive to the presence of trace amounts of moisture; the reaction catalyzed by $K_5CoW_{12}O_{40}$ ·3H₂O appears to be tolerant to large amounts of water in the reaction system.

In order to evaluate the possibility of applying our methodology in a large-scale esterification, we carried out the reaction of octan-1-ol with 3-phenylpropanoic acid starting from 13.0 g (100 mmol) of alcohol. The yield in the ester (entry 6) was almost the same as that of the smallscale (1 mmol) reaction.

The results obtained in transesterification reactions are illustrated in Table 3. Transformations of esters from low to higher homologues and vice versa were achieved efficiently using this procedure. Transesterification of a methyl ester to a *tert*-butyl ester (entries 11 and 14), which is normally problematic, is achieved with this reagent but transesterification with benzyl alcohol did not proceed. While esterification of *o*-toluic acid was not achieved with this reagent, the transesterification of methyl *o*-toluate to butyl *o*-toluate was accomplished with ease.

In conclusion, we have reported herein several noteworthy features of a new catalyst for esterification and transesterification reactions. The reaction proceeds under essentially neutral conditions, and the catalyst is recoverable and reusable. This protocol can be readily applied to large-scale processes with high efficiency and selectivity, making it an economical and environmentally friendly process especially effective for simultaneous esterification and transesterification reactions. Very few catalysts are known to catalyze esterification and transesterification reactions and K₅CoW₁₂O₄₀·3H₂O is one such catalyst that accomplishes both.

$Potassium \ Dodecatangestocobaltate \ Trihydrate \ (K_5 CoW_{12}O_{40}{\cdot}3H_2O)$

CoAc₂ (1.77 g, 0.01 mol) and Na₂WO₄·2H₂O (39.6 g, 0.12 mol) were initially treated with AcOH (5 mL) and H₂O at pH 6.5 to 7.5 to give sodium tungestocobalt(II)ate. The sodium salt was then converted into the potassium salt by treatment with KCl (26.0 g). Finally, the cobalt(II) complex was oxidized to the cobalt(III) complex by K₂S₂O₈ (21.0 g) in H₂SO₄ (2 M, 80 mL). The crystals of K₅CoW₁₂O₄₀·3H₂O were dried at 200 °C. After recrystallization with MeOH, K₅CoW₁₂O₄₀·3H₂O was obtained; yield: 17.5 g (55%); light-blue solid.

Octyl Phenylpropionate; Typical Procedure (Table 2, Entry 3) To a solution of phenylacetic acid (1.36 g, 10 mmol), octan-1-ol (1.30 g, 10 mmol), and catalyst K_5 Co $W_{12}O_{40}$ · $3H_2O$ (0.1 mol%, 0.01

mmol, 32 mg) were heated at 85 °C in toluene (5 mL) for 6 h (Table 2). The progress of the reaction was monitored by TLC. The mixture was filtered to separate the catalyst and the solid material was washed with MeCN (5 mL). The solvent removed under reduced pressure to afford the crude product, which was purified by column chromatography to give the desired carboxylic ester; yield: 2.54 g (93%). The filtered catalyst was reactivated by heating in an oven at 70 °C for 2 h for reuse.

¹H NMR (CDCl₃, 200 MHz): δ = 0.95 (t, *J* = 7.5 Hz, 3 H), 1.23–1.49 (m, 6 H), 1.57–1.71 (m, 6 H), 3.61 (s, 2 H), 4.08–4.21 (m, 2 H), 7.08–7.10 (m, 3 H), 7.12–7.16 (m, 2 H).

All the products in Table 2 are known compounds and were easily identified by comparison of their physical properties with those of authentic samples. Selected analytical data for products are as follows:

Butyl Phenylacetate (Table 2, Entry 1)

¹H NMR (CDCl₃, 200 MHz): δ = 0.95 (t, *J* = 7.5 Hz, 3 H), 1.22–1.48 (m, 2 H), 1.54–1.68 (m, 2 H), 3.58 (s, 2 H), 4.06–4.16 (t, *J* = 6.0 Hz, 2 H), 7.06–7.10 (m, 3 H), 7.14–7.18 (m, 2 H).

2-Methylheptyl Cyclohexanoate (Table 2, Entry 8)

¹H NMR (CDCl₃, 200 MHz): δ = 0.92 (t, *J* = 6.8 Hz, 3 H), 1.25 (d, *J* = 6.0 Hz, 3 H), 1.27–1.35 (m, 12 H), 1.37–1.46 (m, 1 H), 1.52–1.60 (m, 1 H), 2.22 (s, 3 H), 2.53 (t, *J* = 6.5 Hz, 2 H), 2.75 (t, *J* = 6.5 Hz, 2 H), 4.82–4.95 (m, 1 H).

¹³C NMR (CDCl₃, 50 MHz): δ = 14.0, 19.7, 22.5, 25.4, 28.2, 29.1, 30.0, 31.8, 36.0, 38.0, 71.5, 172.4, 206.1.

(Z)-3-Hexenyl 3-Phenylpropanoate (Table 2, Entry 10)

¹H NMR (CDCl₃, 200 MHz): δ = 0.95 (t, J = 7.5 Hz, 3 H), 2.03–2.08 (m, 2 H), 2.15–2.18 (m, 2 H), 2.65 (t, J = 7.8 Hz, 2 H), 2.96 (t, J = 7.8 Hz, 2 H), 4.04 (t, J = 6.0 Hz, 2 H), 5.10–5.18 (m, 1 H), 5.22–5.25 (m, 1 H), 7.08–7.12 (m, 3 H), 7.14–7.18 (m, 2 H).

¹³C NMR (CDCl₃, 50 MHz): δ = 15.0, 20.5, 27.0, 30.6, 35.7, 63.8, 123.8, 126.1, 128.0, 128.5, 134.5, 140.5, 173.2.

| Table 3 | Transesterification | of Carboxylic | Esters | with Alcohols ^a |
|---------|---------------------|---------------|--------|----------------------------|
|---------|---------------------|---------------|--------|----------------------------|

| Entry | $R^1CO_2R^2$ | R ³ OH | Product | Time (h) | Yield (%) ^b |
|-------|---|--|---|----------|------------------------|
| 1 | PhCH ₂ CO ₂ (CH ₂) ₃ Me | MeOH | PhCH ₂ CO ₂ Me | 8 | 91 |
| 2 | PhCH ₂ CO ₂ Me | PhCH ₂ OH | PhCH ₂ CO ₂ CH ₂ Ph | 9 | 90 |
| 3 | PhCH ₂ CO ₂ Me | PhCH ₂ OH | PhCH ₂ CO ₂ CH ₂ Ph | 9 | 86 ^c |
| 4 | 2-HOC ₆ H ₄ CO ₂ (CH ₂) ₂ CHMe ₂ | Me(CH ₂) ₃ OH | 2-HOC ₆ H ₄ CO ₂ (CH ₂) ₃ Me | 6 | 95 |
| 5 | 2-HOC ₆ H ₄ CO ₂ (CH ₂) ₂ CHMe ₂ | PhCH ₂ OH | 2-HOC ₆ H ₄ CO ₂ CH ₂ Ph | 8 | 95 |
| 6 | 2-HOC ₆ H ₄ CO ₂ Me | Me(CH ₂) ₇ OH | 2-HOC ₆ H ₄ CO ₂ (CH ₂) ₇ Me | 7 | 92 |
| 7 | 2-HOC ₆ H ₄ CO ₂ Me | i-PrOH | $2-HOC_6H_4CO_2Pr-i$ | 10 | 90 |
| 8 | $4-CH_3C_6H_4CO_2Me$ | Me ₂ CH(CH ₂) ₂ OH | 4-MeC ₆ H ₄ CO ₂ (CH ₂) ₂ CHMe ₂ | 8 | 89 |
| 9 | PhCH=CHCO ₂ Me | Me(CH ₂) ₃ OH | PhCH=CHCO ₂ (CH ₂) ₃ Me | 7 | 82 |
| 10 | CH ₂ =CH(CH ₂) ₈ CO ₂ Me | Me(CH ₂) ₃ OH | $CH_2 = CH(CH_2)_8 CO_2(CH_2)_3 Me$ | 8 | 74 |
| 11 | Me(CH ₂) ₁₆ CO ₂ Me | t-BuOH | Me(CH ₂) ₁₆ CO ₂ Bu-t | 12 | 91 |
| 12 | Me(CH ₂) ₁₆ CO ₂ Me | PhCH ₂ OH | Me(CH ₂) ₁₆ CO ₂ CH ₂ Ph | 10 | 87 |
| 13 | 3-ClC ₆ H ₄ CO ₂ Et | t-BuOH | 3-ClC ₆ H ₄ CO ₂ Bu-t | 12 | 84 |
| 14 | CH ₂ =CH(CH ₂) ₈ CO ₂ Me | t-BuOH | CH ₂ =CH(CH ₂) ₈ CO ₂ Bu-t | 8 | 80 |
| 15 | EtOCH ₂ CO ₂ Et | O N O O O O H | EtOCH ₂ CO ₂ CH ₂ CH ₂ NPht | 10 | 35 |
| 16 | CICH ₂ CO ₂ Et | O N O O O | CICH ₂ CO ₂ CH ₂ CH ₂ NPht | 15 | 45 |

^a Reaction conditions: 1.0 mmol ester, 1.0 mmol alcohol, 10 mol% catalyst, 85 °C.

^b Isolated yield, average of two runs.

^c Catalyst was reused at least twice.

2-(1,3-Dioxo-1,3-dihydro-2*H*-isoindol-2-yl) 2-Ethoxyacetate; Typical Procedure (Table 3, Entry 15)

A solution of ethyl ethoxy acetate (1.32 g, 10 mmol), 2-(2-hydroxyethyl)-1*H*-isoindole-1,3(2*H*)-dione (1.91 g, 10 mmol), and catalyst $K_5COW_{12}O_{40}$ ·3H₂O (0.1 mol%, 32 mg) was heated at 85 °C in toluene (5 mL) for 10 h. The progress of the reaction was monitored by TLC. The mixture was filtered to separate the catalyst and the solid material was washed with MeCN (5 mL). The solvent was removed under reduced pressure to afford the crude product, which was purified by column chromatography to give the desired carboxylic ester; yield: 0.97 g (35%); mp 54.4–54.7 °C.

¹H NMR (CDCl₃, 200 MHz): δ = 1.20 (t, *J* = 7.0 Hz, 3 H), 3.55 (q, *J* = 7.0 Hz, 2 H), 3.98 (t, *J* = 5.2 Hz, 2 H), 4.07 (s, 2 H), 4.42 (t, *J* = 5.2 Hz, 2 H), 7.75–7.83 (m, 4 H).

All the products in Table 3 are known compounds and were easily identified by comparison of their physical properties with those of authentic samples.

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