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OXIDATIVE COUPLING OF 1,3-DICARBONYL COMPOUNDS BY CERIUM(IV) AMMONIUM NITRATE

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A fast, mild, and highly efficient method for the intermolecular coupling of 1,3-dicarbonyl compounds using cerium ammonium nitrate in $CH_3CNICH_3OHIH_2O$ has been described. The procedure provided a convenient method for the synthesis of 1,4-diketone derivatives with excellent yields (up to 96%) and powerful evidence for the oxidation mechanism mediated by cerium ammonium nitrate.

Keywords: Cerium ammonium nitrate; coupling reaction; 1,3-dicarbonyl compound; radical reaction

INTRODUCTION

Carbon-carbon bond-formation reaction is considered to be one of the most important reactions in the organic synthesis. Carbon-carbon bond formation was usually carried out by coupling the double-bond functions of the compounds, such as coupling of aldehydes,^[1] ketones,^[2] and imines ^[3] with reducing agents including magnesium,^[4] aluminum,^[5] and samarium.^[6] Only a few examples of oxidative reagents in coupling reaction were reported. On the other hand, cerium(IV) ammonium nitrate (CAN), an efficient single-electron-transfer (SET) reagent, was studied in the carbon–carbon bond-forming reactions^[7] and deprotection reactions^[8] extensively. Most recently, Zhang and coworkers^[9] reported that β-ketoesters could be converted to corresponding carboxylic acids using CAN as an oxidative reagent in 42-95% yield. They assumed that the active cation radical **1** was the key intermediate in the oxidation (Scheme 1). We thought that if the cation radical 1 exists in the reaction system, the dimer of 1 could be formed under an appropriate condition, and the dimers are useful intermediates in the synthesis of cyclopentanone and furan derivatives. These encouraged us to explore the intermolecular coupling of 1,3-dicarbonyl compounds using CAN as oxidative reagent to get the dimer of 1. In this article, we

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Scheme 1. The key intermediate in the oxidative reaction.

describe a convenient and highly efficient method for the intermolecular coupling of 1,3-dicarbonyl using CAN as an oxidative reagent to get 1,4-diketone derivatives with excellent yield (up to 96%).

RESULTS AND DISCUSSION

The reaction temperature is critical for the capture of an active intermediate in the reaction. Moreover, the using of excessive CAN in the coupling reaction decreased the desired product.^[10] After many trials, the best result of the coupling reaction was obtained by using acetylacetone (2a) as a typical substrate in the presence of 1.1 eq. of CAN at -20 °C for 15 min, and 80% yield was achieved under these conditions.

With the optimum reaction conditions in hand, the coupled reactions of various benzoyl acetone derivatives and ethyl benzoylacetate derivatives were explored. The results are summarized in Table 1. The results showed that diketones are more reactive than ketoesters, and the coupling rate of diketones is greater than ketoesters. Completing the reaction of diketones needs 15 min, but 4 h was needed for the coupling of ketoesters (Table 1, entries 1–10 and 11–14). In addition, the electronic nature on the phenyl ring of the ketoester had remarkable influence on the yield of the reaction. Better yields were achieved with electron-donating group on the phenyl ring, while the *para*-substituent of electron-withdrawing provided lesser yield (Table 1. entry 12). The substituent position had small effect on the yields of the coupling of diketones. The electron-withdrawing group on the phenyl ring reduced the yield, and the electron-donating group on the phenyl ring improved the yields (Table 1, entries 4, 5, 9, and 10). The substrates with both electron-donating groups and electron-withdrawing groups could achieve satisfying yield. Cross-coupling reaction of diketone and ketoester was unsuccessful (Scheme 2). The cross-coupling reaction gave benzoic acid derivatives, which were determined by gas chromatographic (GC) analysis, and the unreactive ketoester was recovered. The result is reasonable according the reported mechanism.^[9a] One equivalent of CAN first oxidized a diketone to give intermediate 4, and the other equivalent of CAN further oxidized 4 to provide a benzoic acid derivative as the main product. Only the reaction of 2g and 2m, a Cl substituent on the *para*- position of phenyl group, provided the cross-coupling product with 10% yield in the cross-coupling reaction of diketone and ketoester.

Based on the experimental data and related report, $^{[9a,11]}$ the possible mechanism is shown in Scheme 3. The enol of the 1,3-dicarbonyl compound was first oxidized by Ce(IV) to form the cation radical 1. The proton of methene of the diketone has greater acidity than the ketoester, so the diketone could change more easily into 4 than the ketoester, which was further coupled to provide product 3 with lack of enough

Table 1. CAN-mediated oxidative coupling reaction of 1,3-diketone^a



(Continued)



Table 1. Continued

^{*a*}Reactions performed with the 1.1 eq. of CAN in CH₃CN/CH₃OH/H₂O (2/1/1, v/v/v) at -20 °C for 15 min.

^bIsolated yield.

 cReactions performed with the 1.1 eq. of CAN in CH_3CN/CH_3OH/H_2O (2/1/1, v/v/v) at $-20\,^\circ C$ for 4 h.

CAN. The intermediate 4 was formed by oxidizing of diketone at first in the crosscoupling of diketone and ketoester, and the ketoester was not oxidized at this state, so the excessive CAN was further oxidized 4 to give benzoic acid derivative. The internal ligand transfer of nitrate played an important role in the reaction, which



Scheme 2. Cross-coupling of diketones and ketoesters.



Scheme 3. The mechanism of oxidative coupling of 1,3-dicarbonyl by CAN.

led to the completion of the reaction.^[9a] After formation of **5**, which could be transferred to the product **3** under the lack of enough CAN, the preproduct was transferred to product by the action of H_2O of the system, which reduced the by-product, improved the yield, and accelerated the rate of the coupling reaction.

CONCLUSIONS

In conclusion, a fast, mild, and highly efficient method for the conversion of 1,3-dicarbonyl compounds to the corresponding dimers using CAN in CH₃CN/CH₃OH/H₂O has been developed. The procedure provided an alternative convenient route for the synthesis of polycarbonyl compounds by using nontoxic and inexpensive Ce(IV) under mild conditions. Aside from the coupling products, the procedure offered a powerful proof of the oxidation mechanism by CAN. Further exploration of the synthetic utility of this new reaction is under way.

EXPERIMENTAL

Melting points are determined by using an electrothermal melting-point apparatus and are uncorrected. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance 400 spectrometer, and chemical shift values are recorded in δ units (ppm) relative to Me₄Si as internal standard. Elemental analyses are performed on an elemental Vario EL III CHNS analyzer.

General Procedure of CAN-Mediated Oxidative Coupling Reaction of 1,3-Dicarbonyl Compounds

A solution of CAN (3 g, 5.5 mmol) in H₂O (10 mL) was added dropwise to a solution of **2a** (0.512 g, 5 mmol) in CH₃CN (20 mL) and CH₃OH (10 mL) over a period of 5 min at -20 °C. The mixture was stirred at the same temperature for another 10 min, and H₂O was added. The organic layer was separated, and the aqueous layer was extracted with EtOAc (2 × 15 mL). The combined organic phase was washed with H₂O (15 mL) and dried over Na₂SO₄. After removal of the solvent

under reduced pressure, the residue was recrystallized (EtOAc-hexane) to afford a white solid.

3,4-Diacetylhexane-2,5-dione (3a). White solid. Mp 190–191 °C. ¹H NMR (CDCl₃): 16.76 (s, 2H), 2.00 (s, 12H). ¹³C NMR (CDCl₃): 192.6, 108.1, 23.5. Anal. calcd. for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.50; H, 7.18.

3,4-Dibenzoylhexane-2,5-dione (3b)^[12]. White solid. Mp 188–191 °C. ¹H NMR (CDCl₃): 8.19–8.17 (d, J = 8 Hz, 4H), 7.69–7.65 (m, 2H), 7.59–7.55 (m, 4H), 5.92 (s, 2H), 2.08 (s, 6H). ¹³C NMR (CDCl₃): 200.1, 194.8, 136.6, 134.1, 77.3, 77.0, 76.7, 62.5, and 30.6. Anal. calcd. for C₂₀H₁₈O₄: C, 74.52; H, 5.63. Found: C, 74.60; H, 5.65.

3,4-Bis(2-methylbenzoyl)hexane-2,5-dione (3c). White solid. Mp 188–190 °C. ¹H NMR (CDCl₃): 17.3 (s, 2H), 7.22–7.18 (m, 2H), 7.09–7.04 (m, 4H), 6.83–6.81 (m, 2H), 2.38 (s, 6H), 1.44 (s, 6H).¹³C NMR (CDCl₃): 197.3, 188.1, 137.8, 135.1, 131.3, 129.7, 127.6, 124.6, 108.7, 24.9, and 19.0. Anal. calcd. for $C_{22}H_{22}O_4$: C, 75.41; H, 6.33. Found: C, 75.52; H, 6.40.

3,4-Bis(3-methylbenzoyl)hexane-2,5-dione (3d). White solid. Mp 185–188 °C. ¹H NMR (CDCl₃): 7.99–7.95 (m, 4H), 7.47–7.43 (m, 4H), 5.89 (s, 2H), 2.47 (s, 6H), 2.07 (s, 6H). ¹³C NMR (CDCl₃): 200.2, 195.0, 138.9, 136.7, 134.8, 129.6, 128.9, 128.9, 126.5, 62.5, 30.5, and 21.4. Anal. calcd. for $C_{22}H_{22}O_4$: C, 75.41; H, 6.33. Found: C, 75.45; H, 6.45.

3,4-Bis(4-methylbenzoyl)hexane-2,5-dione (3e). White solid. Mp 205–207 °C. ¹H NMR (CDCl₃): 8.07–7.34 (dd, $J_1 = 8$ Hz, $J_2 = 285$ Hz, 8H), 5.86 (s, 2H), 2.45 (s, 6H), 2.07 (s, 6H). ¹³C NMR (CDCl₃): 200.2, 194.2, 145.0, 134.2, 129.7, 129.3, 62.3, 30.4, and 21.71. Anal. calcd. for C₂₂H₂₂O₄: C, 75.41; H, 6.33. Found: C, 75.52; H, 6.44.

3,4-Bis(3-chlorobenzoyl)hexane-2,5-dione (3f). White solid. Mp 176–177 °C. ¹H NMR (CDCl₃): 8.11–8.08 (m, 4H), 7.65–7.63 (m, 2H), 7.55–7.51 (m, 2H), 5.80 (s, 2H), 2.06 (s, 6H). ¹³C NMR (CDCl₃): 199.3, 193.6, 138.2, 135.5, 134.0, 130.4, 129.1, 127.3, 62.7, and 30.4. Anal. calcd. for $C_{20}H_{16}Cl_2O_4$: C, 61.40; H, 4.12. Found: C, 61.38; H, 4.18.

3,4-Bis(4-chlorobenzoyl)hexane-2,5-dione (3g). White solid. Mp 190–193 °C. ¹H NMR (CDCl₃): 17.40 (s, 2H), 7.33–7.27 (dd, $J_1 = 8.8$ Hz, $J_2 = 17.5$ Hz, 8H), 5.78 (s, 2H), 2.07 (s, 6H). ¹³C NMR (CDCl₃): 199.4, 194.7, 137.6, 131.9, 130.6, 129.9, 62.3, and 30.1. Anal. calcd. for C₂₀H₁₆Cl₂O₄: C, 61.40; H, 4.12. Found: C, 61.45; H, 4.08.

3,4-Bis(4-bromobenzoyl)hexane-2,5-dione (3h). White solid. Mp 196–197 °C. ¹H NMR (CDCl₃): 8.05–7.71 (dd, J_1 = 8.6 Hz, J_2 = 127.7 Hz, 8H), 5.79 (s, 2H), 2.04 (s, 6H).¹³C NMR (CDCl₃): 199.5, 193.8, 135.3, 132.4, 130.7, 129.6, 62.4, and 30.4. Anal. calcd. for C₂₀H₁₆Br₂O₄: C, 50.03; H, 3.36. Found: C, 50.12; H, 3.40.

3,4-Bis(4-(trifluoromethyl)benzoyl)hexane-2,5-dione (3i). White solid. Mp 180–183 °C. ¹H NMR (CDCl₃): 17.2 (s, 2H), 7.55–7.33 (dd, $J_1 = 8.2$ Hz,

 $J_2 = 80.0$ Hz, 8H), 2.17 (s, 6H).¹³C NMR (CDCl₃): 195.1, 180.9, 151.5, 142.6, 138.1, 135.7, 127.3, 125.6, 122.3, 110.0, 97.3, 67.9, 66.4, 34.2, 30.3, 26.1, and 21.1. Anal. calcd. for C₂₂H₁₆F₆O₄: C, 57.65; H, 3.52. Found: C, 57.71; H, 3.49.

3,4-Bis(4-fluorobenzoyl)hexane-2,5-dione (3j). White solid. Mp 171–173 °C. ¹H NMR (CDCl₃): 17.4 (s, 2H), 7.42–6.96 (dd, $J_1 = 8.6$ Hz, $J_2 = 151.6$ Hz, 8H), 2.06 (s, 6H).¹³C NMR (CDCl₃): 200.1, 193.1, 167.7, 165.1, 132.1, 131.9, 130.4, 116.4, 116.2, 62.4, 30.5, and 24.9. Anal. calcd. for C₂₀H₁₆F₂O₄: C, 67.04; H, 4.50. Found: C, 67.09; H, 4.46.

Diethyl-2,3-dibenzoylsuccinate (3k). White solid. Mp $127-129 \,^{\circ}$ C. ¹H NMR (CDCl₃): 8.19–7.46 (m, 10H), 5.62 (s, 1H), 5.55 (s, 1H), 4.15–4.12 (m, 2H), 3.98–3.95 (m, 2H), 1.15–1.13 (m, 3H), 0.99–0.95 (m, 3H); ¹³C NMR (CDCl₃): 194.0, 193.1, 167.5, 133.8, 167.1, 133.7, 130.1, 129.4, 129.3, 128.7, 128.6, 128.5, 62.0, 54.2, 53.2, 13.8, 13.6. Anal. calcd. for C₂₂H₂₂O₆: C, 69.10; H, 5.80. Found: C, 68.45; H, 5.63.

Diethyl-2,3-bis(4-methylbenzoyl)succinate (3l). White solid. Mp 164–166 °C. ¹H NMR (CDCl₃): 8.05–7.12 (m, 8H), 5.58 (s, 1H), 5.51 (s, 1H), 4.17–4.11 (m, 2H), 3.99–3.94 (m, 2H), 2.43 (s, 3H), 2.41 (s, 3H), 1.18–1.14 (m, 3H), 0.99–0.96 (m, 3H); ¹³C NMR (CDCl₃): 193.5, 192.6, 167.7, 167.2, 144.7, 144.5, 133.7, 133.3, 130.2, 130.0, 129.6, 129.5, 129.4, 129.3, 129.2, 61.9, 54.0, 53.2, 21.7, 13.8, 13.6. Anal. calcd. for $C_{24}H_{26}O_6$: C, 70.23; H, 6.38. Found: C, 70.20; H, 6.33.

Diethyl-2,3-bis(4-chlorobenzoyl)succinate (3m). White solid. Mp 161–163 °C. ¹H NMR (CDCl₃,): 8.13–7.49 (dd, $J_1 = 6.7$ Hz, $J_2 = 247.1$ Hz, 8H), 5.54 (s, 2H), 4.01–3.96 (m, 4H), 1.01–0.97 (m, 6H); ¹³C NMR (CDCl₃): 192.8, 166.8, 140.4, 134.5, 130.8, 128.9, 62.2, 53.1, 13.6. Anal. calcd. for C₂₂H₂₀Cl₂O₆: C, 58.55; H, 4.47. Found: C, 58.69; H, 4.53.

Diethyl-2,3-bis(4-bromobenzoyl)succinate (3n). White solid. Mp 159–161 °C. ¹H NMR (CDCl₃): 8.04–7.66 (dd, $J_1 = 8.3$ Hz, $J_2 = 146.2$ Hz, 8H), 5.53 (s, 2H), 4.01–3.96 (m, 4H), 1.01–0.98 (t, 6H); ¹³C NMR (CDCl₃): 193.0, 166.7, 134.9, 131.9, 130.9, 129.2, 62.2, 53.0, 13.7. Anal. calcd. for C₂₂H₂₀Br₂O₆: C, 48.91; H 3.73. Found: C, 47.76; H 3.69.

Ethyl-2,3-bis(4-chlorobenzoyl)-4-oxopentanoate. White solid. Mp 208–210 °C. ¹H NMR (CDCl₃): 8.12–8.00 (m, 4H), 7.51–7.29 (m, 4H), 5.82–5.69 (dd, $J_1 = 10.8$ Hz, $J_2 = 42.2$ Hz, 2H), 4.16–4.11 (m, 2H), 2.07 (s, 3H), 1.18–1.12 (m, 3H); ¹³C NMR (CDCl₃): 198.9, 193.2, 192.7, 167.1, 140.8, 134.9, 130.8, 130.7, 130.5, 129.4, 129.1, 128.9, 62.3, 54.1, 45.9, 30.2, 13.8. Anal. calcd. for C₂₂H₂₀Br₂O₆: C, 59.87; H, 4.31. Found: C, 59.83; H, 4.29.

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