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ORIGINAL PAPER

One-pot insertion of chalcones into the benzoylacetone backbone

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Abstract Interaction of 1-phenylbutane-1,3-dione and chalcones in the presence of a base gives, in one step, good to high yields cyclic and unusual acyclic insertion products in ratios which depend on substrate, catalyst, and reaction conditions. All the synthesized compounds are characterized using IR, ^{1}H and ^{13}C NMR spectroscopies, ESI–MS, and single-crystal X-ray diffraction (for one compound) analysis.

Keywords Michael addition · Chalcone · Benzoylacetone · Active methylene compounds

Introduction

The Michael addition of a stabilized carbon nucleophile or a heteroatom-centered nucleophile to electron-deficient olefins is a classical way to construct C–C or C–heteroatom bonds in organic synthesis [1–5]. Active methylene compounds (AMC) are widely used as carbon nucleophiles in the coupling with e.g., chalcone (1,3-diphenyl-2-propen-1-one) to form extended ketones (Scheme 1) [6–9]. An intramolecular cyclization of these coupling products in many instances leads to ring systems with asymmetric carbon atoms, thus allowing an easy preparation of structural motifs found in a variety of natural products [1].

Chalcones are known substrates where different substitution patterns on the two aromatic rings of 1,3-diphenyl-2-propen-1-one are linked by a three carbon α,β-unsaturated carbonyl system which belongs to the flavonoid family [10–12]. Chalcones exhibit a wide spectrum of biological activities including antimicrobial, anticancer, antiprotozoal, antiulcer, and antiinflammatory ones [10, 12]. The coupling products of AMC with chalcones (Scheme 1) not only constitute components of biologically active natural products, but also serve as starting materials for further important organic transformations [13]. Michael additions of AMC to chalcone are usually catalyzed by bases, such as piperidine, CH_3ONa, NaOH, $Ba(OH)_2$, ionic liquids, etc. [14–19]. Due to the presence of bases, the cyclization of the extended ketones (Scheme 1) usually proceeds smoothly giving cyclic products with asymmetric carbon atoms (Routes I and III, Scheme 2). However, to our knowledge, no further ring transformation in such type of syntheses has been reported but was observed in the current study. Hence, herein we report results on the catalyst, solvent, and substituent depending couplings of benzoylacetone with different chalcones.

Experimental section

Materials and instrumentation

All the chemicals were obtained from commercial sources (Aldrich) and used as received. The ^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Bruker System-AV300 (UltraShield^{TM} Magnet) spectrometer operating

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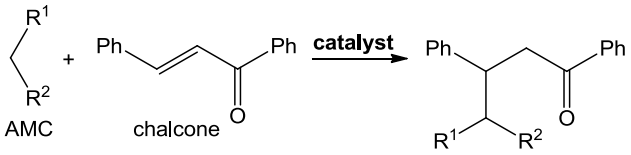


Scheme 1 Michael addition of AMC to chalcone

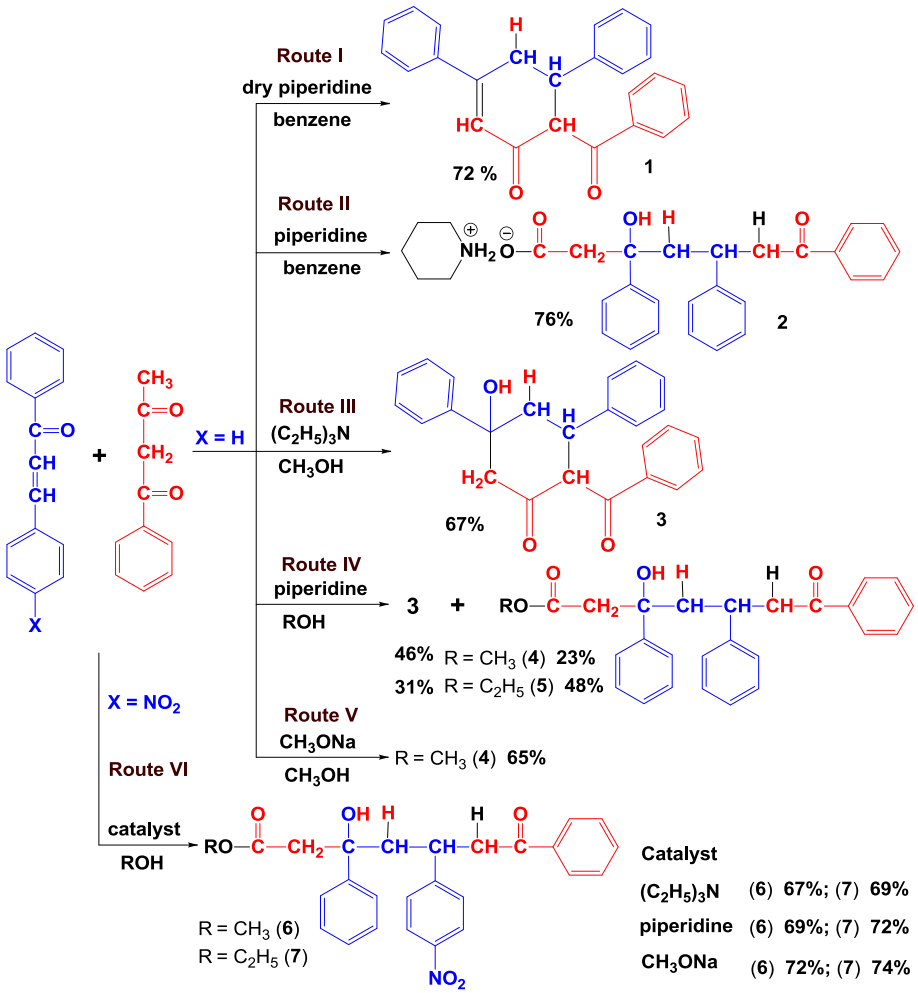
at 300.130 and 75.468 MHz for proton and carbon-13, respectively. The chemical shifts are reported in ppm using tetramethylsilane as the internal reference. Infrared spectra (4000–400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. Carbon, hydrogen, and nitrogen elemental analyses were done using a "2400 CHN Elemental Analyzer" by Perkin Elmer. Electrospray mass spectra were run with an ion trap instrument (Varian 500-MS LC Ion Trap Mass Spectrometer) equipped with an electrospray (ESI) ion source. For electrospray ionization, the drying gas and flow rate were optimized according to the particular sample with 35 p.s.i. nebulizer pressure. Scanning was performed from *m/z* 100 to 1200 in methanol solution. The compounds were observed in the positive mode (capillary voltage = 80–105 V).

Synthesis of 1 and 2

To a solution of 1,3-diphenyl-2-propen-1-one (0.400 g, 1.90 mmol) in benzene (15 mL) 1-phenylbutane-1,3-dione (0.300 g, 1.90 mmol) and 0.05 mL piperidine (dry in the case of **1**) were added in this order and the mixture was stirred at room temperature for 24 h. After completion of the reaction (as monitored by TLC), the solvent was removed under reduced pressure, and the residue was washed with hot water; then, the products were recrystallized from ethanol (yield, 72 and 76 % for **1** and **2**, respectively).

*6′-Benzoyl-1′,6′-dihydro-[1,1′:3′,1″-terphenyl]-5′(2′H)-one (**1**)*

M_p 173 °C; IR (KBr): 2926, 2966, 3006 and 3062 ν(CH), 1610, 1650 and 1676 ν(C=O) cm^{-1}; ^{1}H NMR



Scheme 2 Reaction of 1-phenylbutane-1,3-dione with chalcones

(300.130 MHz, DMSO-d_6): 3.12 (dd, 2H, CH_2, $^2J_{H-H}$ = 16.3 Hz, $^3J_{H-H}$ = 8.2 Hz); 3.91 (t, 1H, CH, $^3J_{H-H}$ = 12.4 Hz); 5.52 (d, 1H, CH, $^3J_{H-H}$ = 12.4 Hz); 6.56 (s, 1H, CH =); 7.1–7.92 (m, 15H_{arom}, 3Ar). ^{13}C NMR (75.468 MHz, DMSO-d_6): 199.4, 197.5, 159.6, 142.7, 138.3, 137.8, 133.7, 130.9, 129.3, 129.1, 128.8, 128.0, 127.2, 126.9, 124.2, 58.2, 43.9, 36.4; MS (ESI): *m/z*: 353.15 $[M + H]^+$.

*Piperidin-1-ium 3-hydroxy-7-oxo-3,5,7-triphenylheptanoate (**2**)*

M_p 108 °C; IR (KBr): 3281 ν(OH), 2856, 2936, 3031, 3053, 3084 and 3104 ν(CH), 1685 ν(C=O) cm^{-1}; ^{1}H NMR (300.130 MHz, DMSO-d_6): 1.14-1.39 (m, 6H, 3CH_2); 2.18 and 2.32 (d-t, 2H, CH_2, $^2J_{H-H}$ = 14.1 Hz, $^3J_{H-H}$ = 8.9 Hz); 2.43 and 2.72 (d, 2H, CH_2, $^3J_{H-H}$ = 8.9 Hz); 3.12 (m, 4H, 2CH_2); 3.48 (m, 1H, CH); 3.64 and 3.12 (d-m, 2H, CH_2, $^3J_{H-H}$ = 15.21 Hz); 6.28 (s, 1H, OH); 6.89-7.69 (m, 15H, 3Ar). ^{13}C NMR (75.468 MHz, DMSO-d_6): 198.2, 169.2, 144.9, 144.3, 136.0, 131.5, 127.3, 127.1, 127.07, 126.4, 125.6, 124.9, 124.2, 74.9, 48.2, 45.6, 45.03, 41.9, 41.4, 36.7, 33.6, 25.2, 24.4, 23.3; MS (ESI): *m/z*: 387.16 $[M\text{-piperidin-1-ium}]^-$.

Synthesis of 3

To a solution of 1,3-diphenyl-2-propen-1-one (0.400 g, 1.90 mmol) in methanol (15 mL) 1-phenylbutane-1,3-dione (0.300 g, 1.90 mmol) and 0.05 mL $(C_2H_5)_3N$ were added in this order. The mixture was then stirred for 24 h while the course of reaction was monitored by TLC. After the reaction completion, the solvent was removed under reduced pressure, and the residue was recrystallized from ethanol to give **3** in 67 % yield.

*2-Benzoyl-5-hydroxy-3,5-diphenylcyclohexanone (**3**)*

M_p 205 °C; IR (KBr): 3420 and 3599 ν(OH), 2922, 2946, 2970, 3025, 3056 and 3084 ν(CH), 1672 ν(C=O) cm^{-1}; ^{1}H NMR (300.130 MHz, DMSO-d_6): 2.00 and 2.64 (d-t, 2H, CH_2, $^2J_{H-H}$ = 13.2 Hz, $^3J_{H-H}$ = 7.5 Hz); 2.41 and 3.52 (d, 2H, CH_2, $^3J_{H-H}$ = 18.2 Hz); 4.10 (t, 1H, CH, $^3J_{H-H}$ = 7.5 Hz); 5.51 (d, 1H, CH, $^3J_{H-H}$ = 10.9 Hz); 5.76 (s, 1H, OH); 7.11–7.92 (m, 15H_{arom}, 3Ar). ^{13}C NMR (75.468 MHz, DMSO-d_6): 207.9, 198.0, 148.4, 143.8, 137.7, 133.6, 129.1, 128.8, 128.5, 128.4, 128.0, 127.7, 127.2, 126.8, 124.9, 76.2, 61.7, 54.1, 46.5, 42.4; MS (ESI): *m/z*: 371.24 $[M + H]^+$.

Synthesis of 4 and 5

Method 1

To 15 mL of methanol (ethanol in the case of **5**) solution of 1,3-diphenyl-2-propen-1-one (0.400 g, 1.90 mmol) 1-phenylbutane-1,3-dione (0.300 g, 1.90 mmol) and 0.05 mL piperidine were added, and the reaction mixture was stirred for 24 h at room temperature and monitored by TLC. After that the solvent was evacuated to 2/3 of its initial volume; the compound **3** precipitated from the thus concentrated solution, being then filtered off and recrystallized from methanol (yield 46 %, or 31 % if ethanol was used as a solvent). In the case of compound **4**, the liquid part of the reaction mixture was completely evacuated and the solid residue was recrystallized from ethanol to give pure product **4** with yield 23 %. Compound **5** with 48 % yield was obtained by the same procedure with ethanol used instead of methanol (Route IV, Scheme 2).

Method 2

To a solution of 1,3-diphenyl-2-propen-1-one (0.400 g, 1.90 mmol) in methanol (15 mL) were added 1-phenylbutane-1,3-dione (0.300 g, 1.90 mmol) and 5 mg CH_3ONa. The mixture was then stirred for 24 h while reaction was monitored by TLC. The solvent was removed under reduced pressure, and the residue was recrystallized from ethanol to give **4** in 65 % yield (Route V, Scheme 2).

Method 3

5 mmol of **3** was dissolved in 15 mL methanol and then 5 mg CH_3ONa was added and the solution was stirred for 24 h at room temperature. After 3 days (as monitored by TLC) the solvent was removed under reduced pressure, and the residue was recrystallized from ethanol to give pure **4** with yield 87 % (Scheme 4).

*Methyl 3-hydroxy-7-oxo-3,5,7-triphenylheptanoate (**4**)*

M_p 134 °C; IR (KBr): 3340 and 3530 ν(OH), 2845, 2896, 2926, 2942, 2951, 3004, 3029, 3060 and 3088 ν(CH), 1680 and 1724 ν(C=O) cm^{-1}; ^{1}H NMR (300.130 MHz, DMSO-d_6): 2.31 (m, 2H, CH_2); 2.83 (s, 2H, CH_2); 3.04 (m, 1H, CH); 3.44 (s, 3H, CH_3O); 3.66 and 3.39 (d-m, 2H, CH_2, $^2J_{H-H}$ = 14.7 Hz); 5.39 (s, 1H, OH); 6.88–7.81 (m, 15H_{arom}, 3Ar). ^{13}C NMR (75.468 MHz, DMSO-d_6): 199.4, 171.2, 146.5, 145.6, 137.0, 133.3, 128.9, 128.4, 128.2, 128.1, 127.6, 126.8, 126.0, 125.9, 75.7, 51.5, 48.9, 48.5, 45.6, 37.7; MS (ESI): *m/z*: 403.27 $[M + H]^+$.

*Ethyl 3-hydroxy-7-oxo-3,5,7-triphenylheptanoate (**5**)*

M_p 200 °C; IR (KBr): 3537 ν(OH), 2907, 2920, 2941, 2963, 2983, 3030, 3055 and 3084 ν(CH), 1675 and 1719 ν(C=O) cm^{-1}; ^{1}H NMR (300.130 MHz, DMSO-d_6): 0.95 (t, 3H, CH_3, $^3J_{H-H}$ = 8.1 Hz); 2.32 (m, 2H, CH_2); 2.81 (d, 2H, CH_2); 3.06 (m, 1H, CH); 3.69-3.40 (d-m, 2H, CH_2,

$^{2}J_{H–H}$ = 14.6 Hz); 3.89 (k, 2H, CH_2O, $^{3}J_{H–H}$ = 8.1 Hz); 5.37 (s, 1H, OH); 6.89–7.79 (m, 15H_{arom}, 3Ar). ^{13}C NMR (75.468 MHz, DMSO-d_6): 199.4, 170.8, 146.5, 145.5, 137.0, 133.3, 128.9, 128.4, 128.2, 128.0, 127.6, 127.2, 126.9, 126.0, 75.8, 59.9, 49.0, 48.7, 45.6, 37.7, 14.3; MS (ESI): *m/z*: 417.09 $[M + H]^+$.

Synthesis of 6 and 7

3-(4-nitrophenyl)-1-phenylprop-2-en-1-one (0.400 g, 1.60 mmol) was dissolved in 15 mL methanol (ethanol in the case of **7**) and refluxed for 5 min, then 1-phenylbutane-1,3-dione (0.260 g, 1.60 mmol) and catalyst (0.05 mL piperidine or $(C_2H_5)_3N$ or 0.050 g CH_3ONa) were added and the reaction mixture was stirred at room temperature for 24 h. After completion of the reaction (as monitored by TLC), the solvent was removed under reduced pressure, and the residue was washed with hot water and recrystallized from ethanol to give pure **6** or **7** with yields, respectively, of 67 and 69 %, with the $(C_2H_5)_3N$ catalyst, 69 and 72 % with piperidine as a catalyst, and 72 and 74 % if CH_3ONa was used.

*Methyl 3-hydroxy-5-(4-nitrophenyl)-7-oxo-3,7-diphenyl-heptanoate (**6**)*

M_p 142 °C; IR (KBr): 3528 ν(OH), 2844, 2900, 2918, 2929, 2941, 2959, 3030, 3066 and 3087 ν(CH), 1675 and 1717 ν(C=O) cm^{-1}; ^{1}H NMR (300.130 MHz, DMSO-d_6): 2.33 (m, 2H, CH_2); 2.81 (s, 2H, CH_2); 3.26 (m, 1H, CH); 3.43 (s, 3H, CH_3O); 3.59 (m, 2H, CH_2); 5.39 (s, 1H, OH); 7.1–7.92 (m, 14H_{arom}, 3Ar). ^{13}C NMR (75.468 MHz, DMSO-d_6): 198.8, 171.1, 154.8, 145.7, 145.4, 136.8, 133.6, 129.1, 128.2, 127.9, 126.7, 125.9, 123.3, 75.3, 51.5, 48.5, 48.2, 45.5, 37.3; MS (ESI): *m/z*: 448.11 $[M + H]^+$.

*Ethyl 3-hydroxy-5-(4-nitrophenyl)-7-oxo-3,7-diphenylheptanoate (**7**)*

M_p 116 °C; IR (KBr): 3499 ν(OH), 2940, 2982, 3027, 3067 and 3110 ν(CH), 1671 and 1722 ν(C=O) cm^{-1}; ^{1}H NMR (300.130 MHz, DMSO-d_6): 0.96 (t, 3H, CH_3, $^{3}J_{H–H}$ = 8.2 Hz); 2.33 (m, 2H, CH_2); 2.79 (s, 2H, CH_2); 3.28 (m, 1H, CH); 3.59 and 2.35 (d-m, 2H, CH_2, $^{3}J_{H–H}$ = 14.7 Hz); 3.88 (k, 2H, CH_2O, $^{3}J_{H–H}$ = 8.2 Hz); 5.36 (s, 1H, OH); 7.1–7.91 (m, 14H_{arom}, 3Ar). ^{13}C NMR (75.468 MHz, DMSO-d_6): 198.8, 170.6, 154.8, 145.7, 145.3, 136.8, 133.6, 129.1, 128.2, 127.9, 126.6, 125.9, 123.3, 75.4, 59.9, 48.6, 48.3, 45.5, 37.3, 14.3; MS (ESI): *m/z*: 462.13 $[M + H]^+$.

Synthesis of 8

338 mg (1 mmol) of ethyl 4-hydroxy-2-oxo-4,6-diphenylcyclohexanecarboxylate was dissolved in 10 mL of methanol and 5 mg of CH_3ONa was added to this solution. Reaction mixture was stirred at room temperature for 24 h (as monitored by TLC). Then the solvent was removed under reduced pressure, and the resulting precipitate of **8** was filtrated off and washed with ethanol (yield, 79 %).

*Ethyl 5′-oxo-2′,3′,4′,5′-tetrahydro-[1,1′:3′,1′′-terphenyl]-4′-carboxylate (**8**)*

M_p 164 °C; IR (KBr): 2903, 2946, 2985, 3031 and 3061 ν(CH), 1606, 1658 and 1735 ν(C=O) cm^{-1}; ^{1}H NMR (300.130 MHz, DMSO-d_6): 0.89 (t, 3H, CH_3, $^{3}J_{H–H}$ = 8.3 Hz); 3.05 (m, 2H, CH_2); 3.48 (t, 1H, CH, $^{3}J_{H–H}$ = 8.3 Hz); 3.89 (q, 2H, CH_2, $^{3}J_{H–H}$ = 8.3 Hz); 4.11 (d, 1H, CH, $^{3}J_{H–H}$ = 11.1 Hz); 3.56 (s, 1H, CH =); 7.23–7.48 (m, 10H, 2Ar). ^{13}C NMR (75.468 MHz, DMSO-d_6): 194.8, 169.8, 159.8, 141.9, 137.7, 130.9, 129.3, 128.9, 128.3, 127.6, 126.9, 123.3; MS (ESI): *m/z*: 321.14 $[M + H]^+$.

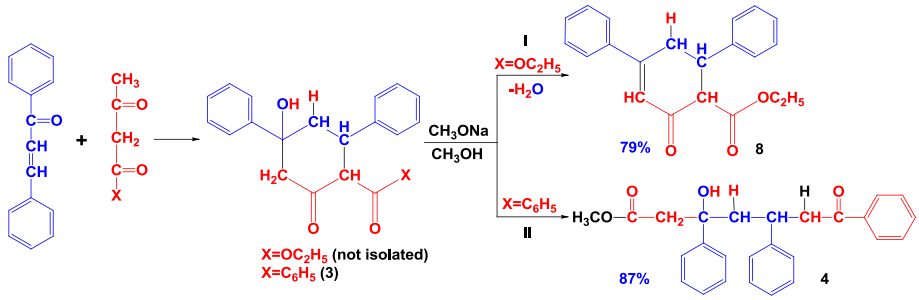
X-ray structure determination

A crystal of **5** was immersed in cryo-oil, mounted in a Nylon loop, and the intensity data were collected at 296 K on a Smart Apex II diffractometer using Mo Kα radiation (λ = 0.71073 Å). The diffraction experiments were carried out on a Bruker APEX II CCD diffractometer. The program SHELXTL [20] was used for collecting frames of data, indexing reflections, and for the determination of the lattice parameters, SAINTP [21]—for integration of the intensity of reflections and scaling, SADABS [22]—for absorption correction, and SHELXTL [20]—for the space group and structure determination, least-squares refinements on F_2. The crystallographic details are summarized in Table (Electronic Supplementary Information). Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication, CCDC (966239) **5**. Copies of this information may be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion

The reactions of chalcones with 1-phenylbutane-1,3-dione were performed in the presence of different solvents (benzene, methanol, and ethanol) and catalysts, such as piperidine, $(C_2H_5)_3N$ and CH_3ONa (Scheme 2). It was observed that in majority of cases the type of reaction products and their yield strongly depend on the solvents used and basicity of catalysts. For instance, alcohols play a dual role as solvents and nucleophilic agents in the synthesis of the acyclic compounds **4**–**7**, however, the yields of the products are

Scheme 3 CH_3ONa-catalyzed dehydration (I) and ring opening (II)



lower in alcoholic medium than in benzene (Routes I, II, and IV, Scheme 2). Moreover, the yield of the acyclic product is higher in ethanol (48 %, synthesis of **5**) than in methanol (23 %, synthesis of **4**) for the piperidine-catalyzed reaction of 1-phenylbutane-1,3-dione with chalcone (Route IV). On the other hand, the found unusual fragmentation of 1-phenylbutane-1,3-dione depends on the basic properties of catalysts: in the presence of more basic CH_3ONa only the insertion product **4** was obtained, while in piperidine compounds **3** and **4**, and in $(C_2H_5)_3N$ exclusively the cyclic product **3** were isolated (Routes III–V). Purity of catalysts is also important in this reaction: when unpurified piperidine was used as a catalyst, only the acyclic compound **2** was isolated (Rote II, Scheme 2), which clearly shows a role of water in the ring opening in compound **1**, and stabilization of this salt. However, when 3-(4-nitrophenyl)-1-phenylprop-2-en-1-one is used as a starting material, result of the reaction is the same, i.e., an acyclic product with unusual insertion of the chalcone into the backbone of benzoylacetone is formed (Route VI, Scheme 2). This fact is possibly related to the higher electron-accepting ability of $–NO_2$ (its Hammett's σ_p constant [23] is 0.78). It should be noted that, more electron-donating group attached in chalcone moiety, such as $–OCH_3$ ($\sigma_p = -0.27$) provides same products as observed in the case of unsubstituted chalcone.

If other AMCs, such as pentane-2,4-dione, 1,3-diphenylpropane-1,3-dione, and ethyl 3-oxobutanoate were used instead of 1-phenylbutane-1,3-dione, the formation of acyclic products with the unusual fragmentation of diones was not observed. Hence, the found insertion most probably occurs through the formation of the cyclic products of the Michael addition. This is, additionally, proved by interaction of the cyclic products with alcohols in the presence of a strong base, such as CH_3ONa (Scheme 3). In this case, replacement of $–OC_2H_5$ group by $–C_6H_5$ in the cyclic substrate (in the synthesis of **4**) leads to a ring opening reaction. The observed difference in behavior can be explained by different electron-withdrawing abilities of the substituents (values of Hammett's σ_p constant [23] are -0.24 for OC_2H_5 and -0.01 for C_6H_5) and bulkiness of phenyl ring.

The structures of all the obtained products were deduced from their IR, ESI–MS, ^{1}H and ^{13}C NMR spectra, and

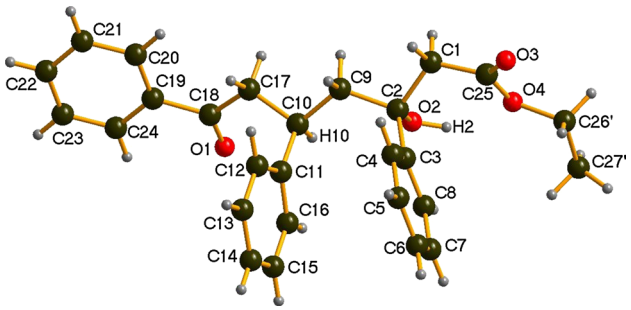
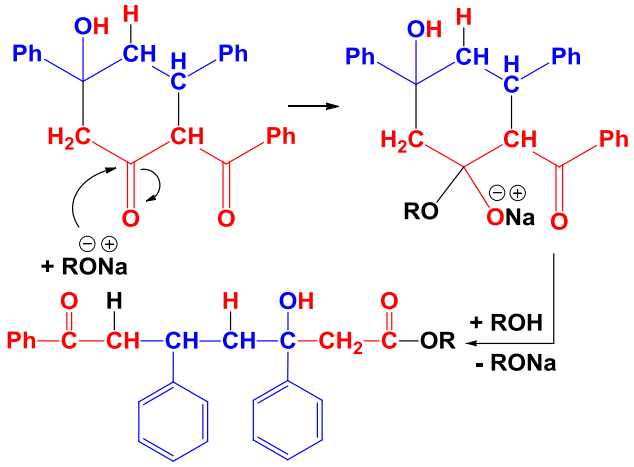


Fig. 1 X-ray structure of compound 5

X-ray diffraction analysis of compound **5** (Fig. 1). The mass spectra of these compounds displayed molecular ion peaks at the appropriate *m/z* (%) values. The IR spectrum of **1**–**8** showed two bands at 2844–3110 and 1606–1685 cm^{-1} due to vibrations of the CH and C=O groups, respectively, and ester carbonyl at 1717–1735 cm^{-1} (for **4**–**8**), while ν(OH) of **2**–**7** reveal at ca. 3281–3599 cm^{-1}. ^{1}H-NMR spectra of **2**–**7** in dimethylsulfoxide-d^6 solution at room temperature show a resonance at δ 5.36–6.28, which can be assigned to the proton of the −OH group. The C<u>H</u> protons of **1**, **3,** and **8** were visible as a triplet at δ 3.91 (J = 12.4 Hz), 4.10 (J = 7.5 Hz), 3.48 (J = 8.3 Hz) and doublets at δ 5.52 (J = 12.4 Hz), 5.51 (J = 10.9 Hz) and 4.11 (J = 11.1 Hz), respectively. The ^{13}C resonance signals for the carbonyl groups were seen at δ 199.4 and 197.5 (for **1**), 198.2 (for **2**), 207.9 and 198.0 (for **3**), 199.4 (for **4**), 199.4 (for **5**), 198.8 (for **6**), 198.8 (for **7**), 194.8 (for **8**). The resonance signals at δ 169.2, 171.2, 170.8, 171.1, 170.6, and 169.8 for **2**, and **4**–**8**, respectively, were attributed to the ester carbonyls. All the other ^{13}C resonance signals are also in agreement with the designated structures. Additionally, a molecular structure of **5** (Fig. 1) was determined by single-crystal X-ray analysis, confirming unambiguously the structures and stereochemistry of the products.

The following mechanism of the encountered unusual insertion can be suggested based on the obtained results. On the first stage, reaction of 1,3-diphenyl-2-propen-1-one with 1-phenylbutane-1,3-dione in the presence of CH_3ONa gives cyclic product **3** (Scheme 2), which undergoes



Scheme 4 Proposed mechanism for ring opening in 3

nucleophilic attack of CH_3ONa leading to a tetrahedral intermediate, which is further transformed to a acyclic compound (Scheme 4). The regeneration of sodium methoxide completes the catalytic cycle.

Conclusions

In summary, we have found that 1-phenylbutane-1,3-dione can undergo an unusual fragmentation upon the Michael reaction with chalcones which insert into its backbone. The found transformation depends on basicity of the catalysts used. Thus, no fragmentation was observed when $(C_2H_5)_3N$ was applied as a catalyst, while in the presence of piperidine and CH_3ONa the acyclic insertion products were isolated. To our knowledge, this is the first report on such direct insertion reaction of chalcones into AMCs. Another notable feature of the reaction is the found one-step one-pot combination of three substrates in one new rather intricate product with multiple stereogenic carbon atoms. The insertion products can possess biological activities similar to chalcones [10–12] or serve as a useful tool for the construction of new coordination and supramolecular architectures [24]. Further study of reactants and conditions can widen the scope of the found interesting one-step one-pot transformation.

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