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Esra Findik [a] , Yakup Budak [a] & Mustafa Ceylan [a]
[a] Department of Chemistry , Faculty of Arts and Sciences, Gaziosmanpasa University , Tokat, Turkey
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Cyclohexenones Through Regioselective Addition of 1,3-Dicarbonyl Compounds to Terpenoid-Like Bischalcones

Esra Findik, Yakup Budak, and Mustafa Ceylan
Department of Chemistry, Faculty of Arts and Sciences, Gaziosmanpasa University, Tokat, Turkey

Abstract: Terpenoid-like bischalcones (**3** and **4**) were synthesized from the reaction of α- and β-ionones and benzaldehydes in excellent yields. The Michael addition of 1,3-dicarbonyl compounds to bischalcones (**3** and **4**) resulted in the formation of cyclohexenones derivatives (**10a–d** and **14a, b**) via regioselective addition of 1,3-dicarbonyls and then cyclization.

Keywords: Cyclization, cyclohexenones, regioselective addition, terpenoid-like bischalcone

1,5-Diaryl-1,4-pentadien-3-ones (bischalcones) are important intermediates and raw materials widely used as precursors to drugs,[1] nonlinear optical materials, organometallic materials,[2,3] and polymers.[4] The Michael reaction of bischalcones with active methylene compounds such as 1,3-dicarbonyl compounds has been the subject of many investigations.[5–9] It is known that a weak base or acid such as piperidine[10] or phosphorustrichloride[11] often affords open-chain adducts, whereas cyclic products have been obtained in the presence of sodium methoxide or sodium hydroxide.[12] Particularly, the products of these cyclic reactions are of interest in terms of their stereochemistry and as starting materials for the synthesis of compounds with possible biological activity.

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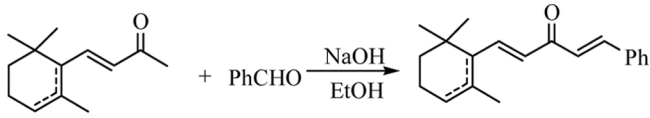
Address correspondence to Esra Findik, Department of Chemistry, Faculty of Arts and Sciences, Gaziosmanpasa University, 60250 Tokat, Turkey. E-mail: mceylan@gop.edu.tr

Reddy et al.[13] have reported that the synthesis of 1,1-disubstituted-2, 6-diarylcyclohexane-4-ones was carried out in moderate to good yields via double Michael addition of bis-chalcone with active methylene compounds in the presence of sodium methoxide. Addition, the Michael reaction of chalcones with 1,3-dicarbonyl compounds may be exploited with the view of obtaining highly functionalized cyclohexene derivatives but is more commonly used for the preparation of 3,5-diaryl-6-substituted cyclohexenones. The mentioned cyclohexenones are efficient synthons in benzoselenadiazoles and benzothiadiazoles,[14] benzopyrazoles and benzisoxazoles,[15,16] and carbazole derivatives.[17]

In this study, we report synthesis of cyclohexenone derivatives by regioselective Michael addition of 1,3-dicarbonyl compounds to bischalcones (**3** and **4**), the latter which were obtained by intramolecular Knoevenagel condensation of the methyl group in 1,3-dicarbonyl compounds. The formation of these products was confirmed by infrared (IR) and ^{1}H NMR spectral studies.

The terpenoid-like bischalcones **3** and **4** were synthesized from the reaction of α- and β-ionones with the benzaldehyde in yields of 90% and 89%, respectively (Scheme 1). The reactions were performed in the presence of aqueous NaOH in ethanol (EtOH) at room temperature for 3 h. The compounds **3** and **4** are best known in the literature.[18–22]

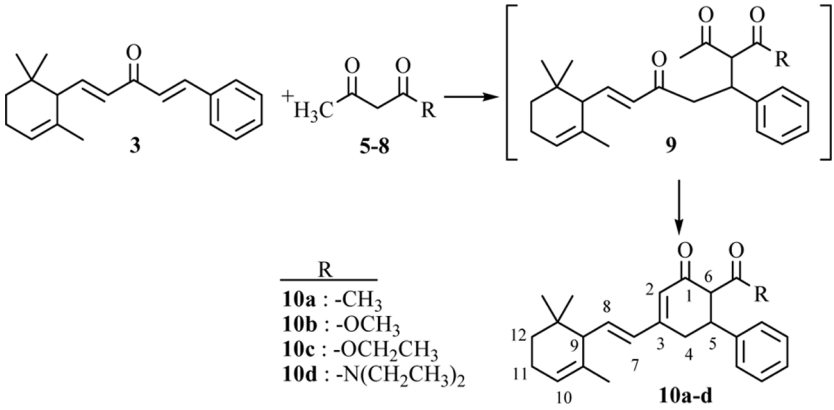
The reaction of chalcones and bischalcones with 1,3-dicarbonyl compounds is known to lead to three structurally diverse types of compounds, depending on the experimental conditions employed: pyrylium salts,[23] Michael addition products,[24] and cyclohexenone derivatives. The catalyst plays a key role in directing the reaction to different end products. The basic catalyst would turn the intermediate Michael addition product into cyclohexenones through the intramolecular cyclocondensation of the methyl group originating from 1,3-dicarbonyl compounds and the ketone function of the initial α,β-unsaturated system.[25] In this research, acetylacetone (**5**), methyl acetoacetate (**6**), ethyl acetoacetate (**7**), and N,N-diethyl-3-oxobutanamide (**8**) were chosen as 1,3-dicarbonyl compounds. The reaction of **3** with 1,3-dicarbonyl



1 = α-ionone
2 = β-ionone

3
4

Scheme 1. Synthesis of bischalcones.



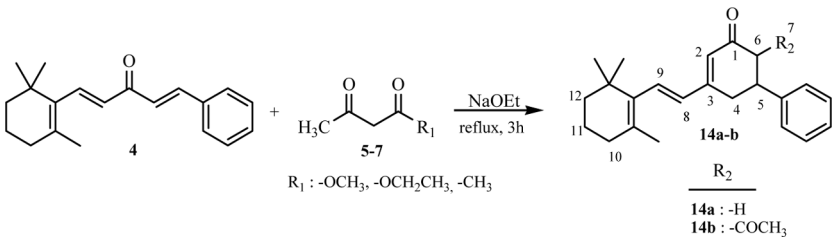
Scheme 2. Addition of 1,3-dicarbonyls to bischalcone (**3**).

compounds **5**–**8** in basic medium resulted in the formation 3,5,6-trisubstituted cyclohexenones derivatives (**10a–d**) by means of an intermediate Michael adduct, as outlined in Scheme 2.

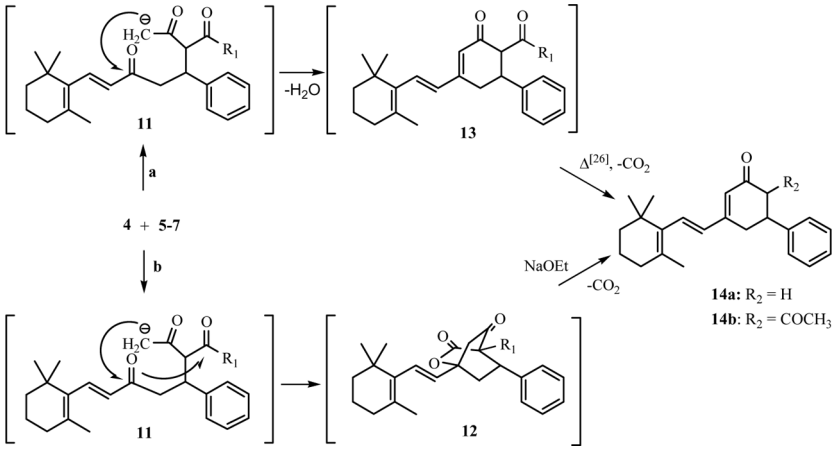
The reaction of **4** with acetylacetone (**5**), methyl acetoacetate (**6**), and ethyl acetoacetate (**7**) in the same conditions gave the 3,5-disubstituted cyclohexenone **14a** and 3,5,6-trisubstituted cyclohexenone **14b,** different from that of **3**.

Control of selectivity, for example, chemo- and regioselectivity, is among the most important objectives in organic chemistry. In this reaction, 1,3-dicarbonyl compounds may be added to two sides (phenyl side or cyclohexenyl side) of bischalcones **3** and **4**. It was observed that the 1,3-dicarbonyl compounds were added as regioselective from the phenyl side of bischalcones **3** and **4** (Scheme 3).

The formation of compound **14a** may be explained by two different mechanisms, depicted in Scheme 4. Path a: Compound **13** converted to compound **14a** by elimination of CO_2, and EtOH, and/or MeOH effect



Scheme 3. Addition of 1,3-dicarbonyls to bischalcone (**4**).



Scheme 4. Formation mechanism of cyclohexanone derivatives (**14a–b**).

of base and temperature.[26] Path b: Lactone compound **12** may be occurring by the intramolecular esterification of intermediate **11** and elimination of CO_2 from **12** (acting base) to give **14a**.

The structure of cyclohexenone derivatives **10a–d** and **14a, b** were elucidated by spectroscopic studies (IR, ^1H and ^{13}C NMR, elemental analysis) and comparison with literature data.

In conclusion, the reaction of bischalcones with 1,3-dicarbonyl compounds in the presence of sodium ethoxide has been shown to afford cyclohexenone derivatives via Michael addition followed by intramolecular cyclocondensation.

EXPERIMENTAL

Instruments

IR spectrums (KBr or liquid) were recorded on a Jasco Fourier Transform (FT) IR-430 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Brucker Avance III instrument. Internal standards were tertramethylsilane (TMS, δ 0.00) for ^1H NMR and $CDCl_3$ (δ 77.0) for ^{13}C NMR spectroscopy. *J* values are given in hertz. The multiplicities of the signals in the ^1H NMR spectra are abbreviated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad), and combinations thereof. Elemental analyses were obtained from a LECO CHNS 932 elemental analyzer.

Reagents α-ionone, β-ionone, benzaldehyde, and 1,3-dicarbonyl compounds were commercial products of highest reagent grade.

Synthesis of Bischalcones 3 and 4

A solution of NaOH (0.26 g, 6.5 mmol) in water was added to a stirred solution of ionone (0.5 g, 2.6 mmol) and benzaldehyde (2,6 mmol) in ethanol (10 ml) and stirred at room temperature for 3 h. The reaction was complete; the mixture was diluted with $CHCl_3$, treated with HCl solution (10%), and washed with water. The organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated. The crude product was chromatographed on a silica-gel column, eluting with $CHCl_3$/petroleum ether (2:8).

1-Phenyl-5-(2,6,6-trimethylcyclohex-2-enyl)penta-1,4-dien-3-one (**3**)

Viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.66$ (d, $J = 16$ Hz, 1H, H1, A part of AB system), 7.55–7.54 (m, 2H, ArH), 7.35–7.34 (m, 3H, ArH), 6.99 (d, $J = 16$ Hz, 1H, H2, B part of AB systym), 6.83 (dd, $J = 15.6$, 9.6 Hz, 1H, H5, A part of AB system), 6.39 (d, $J = 15.6$ Hz, 1H B part of AB system, H4), 5.48 (m, as if brs, 1H), 2.32 (d, $J = 9.6$ Hz, 1H), 1.58 (s, 3H), 1.54–2.45 (m, 2H), 1.24–1.18 (m, 2H), 0.93 (s, 3H), 0.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 188.76$, 148.74, 143.0, 134.81, 131.96, 130.54, 130.34, 128.88 (2C), 128.30 (2C), 124.77, 122.63, 54.52, 32.62, 31.18, 27.89, 26.85, 23.06, 22.91. IR (liquid): 2955, 2915, 1655, 1623, 1598, 1338, 989, 794, 757 cm^{-1}. Anal. calcd. for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.42; H, 8.38.

1-Phenyl-5-(2,6,6-trimethylcyclohex-1-enyl)penta-1,4-dien-3-one (**4**)

Viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.64$ (d, $J = 16$ Hz, 1H, H1, A part of AB system), 7.55–7.52 (m, 3H, 2ArH and H5), 734–7.33 (m, 3H, ArH), 6.99 (d, $J = 16$ Hz, 1H, H2, B part of AB system), 6.47 (d, $J = 16$ Hz, 1H, B part of AB system, H4), 2.06–2.04 (m, 2H), 1.80 (s, 3H), 1.61–1.59 (m, 2H), 1.48–1.46 (m, 2H), 1.09 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 188.21$, 142.92, 142.63, 136.61, 136.48, 134.89, 130.28, 129.56, 128.88 (2C), 128.27 (2C), 125.66, 39.69, 34.14, 33.69, 28.87 (2C), 21.89, 19.08. IR (liquid): 2958, 2930, 2865, 1671, 1653, 1612, 1449, 1333, 1088, 982, 786, 758 cm^{-1}. Anal. calcd. for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.74; H, 8.47.

General Procedure for Synthesis of Cyclohexenone Derivatives (10a–d and 14a, b)

Bischalcone (**3–4**) (1.78 mmol) and 1,3-dicarbonyl (**5–8**) (1.78 mmol) were refluxed 3 h in 10–15 mL ethanol in the presence of sodium ethoxide (0.1 mmol). Water was added to the mixture and extracted with EtOAc (3×20 mL), dried over anhydrous Na_2SO_4, and evaporated. Crude products were purified by column chromatography on silica gel or preparative thin-layer chromatography (TLC; 20×20 cm plates, 2 mm thick) using *n*-hexane/EtOAc (9:1) as eluent.

6-Acetyl-5-phenyl-3-(2-(2,6,6-trimethylcyclohex-2-enyl)vinyl) cyclohex-2-enone (**10a**)

Yield: 78%; viscous oil. IR ν (KBr): 3085, 3061, 3025, 2957, 2918, 2867, 1660, 1624, 1453, 1382, 1363, 1292, 1252, 1216, 970, 755, 700, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.39–7.25$ (m, 5H), 6.26 (d, $J = 15.6$ Hz, 1H, H7), 6.09–6.02 (m, 2H, H8 and H2), 5.47 (m, as if brs, 1H, H10), 3.35–3.32 (m, 2H, H4), 2.89–2.81 (m, 1H, H5), 2.72–2.68 (m, 1H, H6), 2.26 (d, $J = 9.2$ Hz, Hz, 1H, H2), 2.02 (s, 3H, -CH_3) 1.60 (s, 3H, –CH_3), 1.42–1.37 (m, 2H, H11), 1.23–1.16 (m, 2H, H12), 0.94 (s, 3H, –CH_3), 0.83 (s, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 199.66$, 156.32, 143.48, 140.39, 132.03, 128.97, 128.89, 128.81, 127.31, 126.95, 126.82, 126.53, 122.68, 55.11, 44.53, 40.74, 38.99, 33.52, 32.61, 31.33, 27.90, 26.88, 23.03. Anal. calcd. for $C_{25}H_{30}O_2$: C, 82.83; H, 8.34; O, 8.83. Found: C, 82.75; H, 8.29; O, 8.74.

Methyl 2-Oxo-6-phenyl-4-(2-(2,6,6-trimethylcyclohex-2-enyl)vinyl)cyclohex-3-ene-carboxylate (**10b**)

Yield: 81%; yellowish liquid. IR ν (KBr): 3086, 3062, 2954, 2916, 1668, 1624, 1455, 1374, 1240, 1115, 1096, 971, 760, 732, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.37–7.26$ (m, 5H), 6.24 (d, $J = 15.6$ Hz, 1H, H7), 6.07–6.0 (m, 2H, H8 and H2), 5.46 (m, as if brs, 1H, H10), 3.75–3.68 (m, 2H, H4), 3.57 (s, 3H, -OCH_3), 2.89–2.84 (m, 1H, H5), 2.65–2.56 (m, 1H, H6), 2.26 (d, $J = 9.6$ Hz, 1H, H9), 1.57 (s, 3H, –CH_3), 1.44–1.36 (m, 2H, H11), 1.22–1.17 (m, 2H, H12), 0.92 (s, 3H, –CH_3), 0.82 (s, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 194.24$, 169.87, 156.22, 141.36, 141.24, 132.66, 131.45, 128.87, 127.49, 127.23, 125.20, 122.14, 59.96, 59.89, 55.13, 52.01, 43.57, 33.28, 32.64, 31.28, 27.96, 26.79, 23.00. Anal. calcd. for $C_{25}H_{30}O_3$: C, 79.33; H, 7.99; O, 12.68. Found: C, 79.35; H, 7.91; O, 12.63.

Ethyl-2-oxo-6-phenyl-4-(2-(2,6,6-trimethylcyclohex-2-enyl)vinyl)cyclohex-2-enone (**10c**)

Yield: 70%; yellowish liquid. IR ν (KBr): 3086, 3062, 2958, 2916, 1666, 1625, 1455, 1381, 1336, 1291, 1258, 970, 757, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.33–7.29$ (m, 5H), 6.24 (d, $J = 15.6$ Hz, 1H, H7), 6.07–6.03 (m, 2H, H8 and H2), 5.45 (m, as if brs, 1H, H10), 4.00 (q, $J = 7.1$ Hz, 2H, $\underline{CH_2}CH_3$), 3.73–3.64 (m, 2H, H4), 2.89–2.83 (m, 1H, H5), 2.67–2.56 (m, 1H, H6), 2.26 (d, $J = 9.85$ Hz, 1H, H9), 1.59 (s, 3H, $-CH_3$); 1.44–1.37 (m, 2H, H11), 1.21–1.17 (m, 2H, H12), 1.01 (t, $J = 7.1$ Hz, 3H, $-CH_2\underline{CH_3}$), 0.92 (s, 3H, $-CH_3$), 0.81 (s, 3H, $-CH_3$); ^{13}C NMR (100 MHz, $\underline{C}DCl_3$): $\delta = 194.20$, 169.24, 157.00, 141.24, 141.10, 132.63, 131.56, 128.84, 128.76, 127.43, 127.37, 125.35, 122.12, 55.13, 55.08, 43.74, 33.32, 32.63, 32.60, 32.32, 27.95, 26.84, 23.01, 22.93. Anal. calcd. for $C_{26}H_{32}O_2$: C, 82.94; H, 8.57; O, 8.50. Found: C, 82.98; H, 8.61; O, 8.41.

N,N-Diethyl-2-oxo-6-phenyl-4-(2-(2,6,6-trimethylcyclohex-2-enyl)vinyl)cyclohex-3-enecarboxamide (**10d**)

Yield: 75%; yellowish liquid. IR ν (KBr): 3086, 3062, 2965, 2930, 2896, 1661, 1626, 1454, 1381, 1362, 1280, 1211, 1131, 1099, 1078, 971, 756, 701, 666 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.34–7.20$ (m, 5H), 6.22 (d, $J = 15.6$ Hz, 1H, H7), 6.06–6.00 (m, 2H, H8 and H2), 5.43 (m, as if brs, 1H, H10), 3.93–3.78 (m, 2H, H4), 3.38–3.32 (m, 4H, $-N\underline{CH_2}CH_3$), 2.91–2.85 (m, 1H, H5), 2.73–2.65 (m, 1H, H6), 2.25 (d, $J = 9.4$ Hz, 1H, H9), 1.56 (s, 3H, $-CH_3$), 1.42–1.37 (m, 2H, H11), 1.19–1.16 (m, 2H, H12), 0.89 (s, 3H, $-CH_3$), 0.84 (t, $J = 6.8$ Hz, 6H, $-NCH_2\underline{CH_3}$), 0.79 (s, 3H, $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 195.63$, 168.19, 156.02, 142.06, 140.79, 132.73, 131.75, 128.49, 127.72, 127.08, 125.93, 122.03, 56.36, 55.08, 43.49, 42.77, 40.59, 32.57, 32.08, 31.34, 27.90, 26.82, 22.91, 22.88, 14.48, 12.71. Anal. calcd. for $C_{28}H_{37}NO_2$: C, 80.15; H, 8.89; O, 7.63; N, 3.34. Found: C, 80.11; H, 8.78; O, 7.68; N, 3.29.

5-Phenyl-3-(2-(2,6,6-trimethylcyclohex-1-enyl)vinyl)cyclohex-2-enone (**14a**)

Yield: 68%; yellowish liquid. IR ν (KBr): 3086, 3061, 2956, 2928, 2864, 1660, 1607, 1454, 1379, 1360, 1287, 1257, 970, 757, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.38–7.32$ (m, 5H), 6.66 (d, $J = 16.2$ Hz, 1H, H9

or H8), 6.26 (d, $J = 16.2$ Hz, 1H, H9 or H8), 6.06 (s, 1H, H2), 3.76–3.71 (m, 2H, H4), 2.98–1.93 (m, 1H, H5), 2.71–2.64 (m, 2H, H6), 1.74 (s, 3H, $-CH_3$), 1.63–1.59 (m, 4H, H10 and H11), 1.48–1.45 (m, 2H, H12), 1.02 (s, 6H, $2 \times -CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 194.19$, 169.36, 156.50, 141.30, 136.97, 136.24, 133.31, 132.67, 128.79, 127.42, 125.39, 44.08, 39.50, 34.15, 33.21, 32.97, 28.95, 28.91, 21.81, 19.01. Anal. calcd. for $C_{23}H_{28}O$: C, 86.20; H, 8.81; O, 4.99. Found: C, 86.24; H, 8.87; O, 4.89.

6-Acetyl-5-phenyl-3-(2-(2,6,6-trimethylcyclohex-1-enyl)vinyl) cyclohex-2-enone (**14b**)

Yield: 73%; yellowish liquid. IR ν (KBr): 3088, 3064, 2966, 2932, 1653, 1622, 1455, 1379, 1295, 1258, 975, 760, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.42$–7.36 (m, 2H), 7.34–7.30 (m, 3H), 6.66 (d, $J = 16.2$ Hz, 1H, H9 or H8), 6.26 (d, $J = 16.2$ Hz, 1H, H9 or H8), 6.03 (s, 1H, H2), 3.47–3.33 (m, 2H, H4), 2.94–2.89 (m, 1H, H5), 2.60–2.56 (m, 1H, H6), 2.05 (s, 3H, $-CH_3$), 1.74 (s, 3H, $-CH_3$), 1.64–1.56 (m, 4H, H10 and H11), 1.49–1.46 (m, 2H, H12), 1.03 (s, 3H, $-CH_3$), 1.02 (s, 3H, $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 199.54$, 156.68, 143.58, 137.06, 135.41, 133.27, 132.74, 128.83, 128.72, 127.05, 126.87, 126.48, 44.54, 40.74, 39.49, 34.22, 33.21, 33.14, 28.94, 28.91, 21.78, 19.01. Anal. calcd. for $C_{25}H_{30}O_2$: C, 82.83; H, 8.34; O, 8.83. Found: C, 82.60; H, 8.40; O, 8.78.

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