Short Communication

CYCLOHEXENONES THROUGH ADDITION OF ETHYL ACETOACETATE TO CHALCONES DERIVED FROM 2-ACETYLTHIOPHENE

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Abstract

Nine new ethyl 6-aryl-4-(2-thienyl)cyclohex-3-en-2-one-1-carboxylates, valuable intermediates in the synthesis of fused heterocycles, have been prepared through NaOH-catalyzed cyclocondensation of 3-aryl-1-(2-thienyl)prop-2-en-1-ones with ethyl acetoacetate.

Key words: chalcone, Michael addition, cyclocondensation, cyclohexenones

Introduction

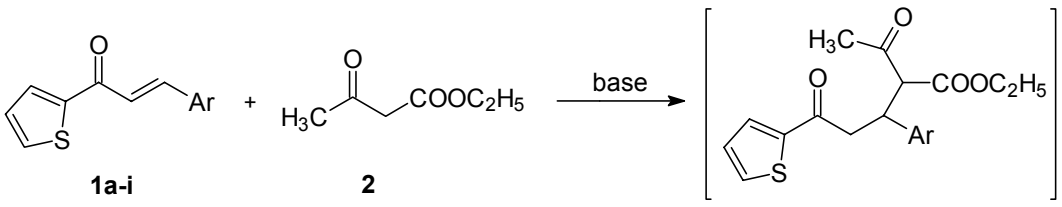
Chalcones and the corresponding heterocyclic analogs are valuable intermediates in organic synthesis[1] and exhibit a multitude of biological activities.[2] From a chemical point of view, an important feature of chalcones and their heteroanalogs is the ability to act as activated unsaturated systems in conjugated addition reactions of carbanions in the presence of basic catalysts.[3,4] This type of reaction may be exploited with the view of obtaining highly functionalized cyclohexene derivatives,[5] but is more commonly used for the preparation of 3,5-diaryl-6-carbethoxycyclohexenones *via* Michael addition of ethyl acetoacetate. The mentioned cyclohexenones are efficient synthons in building spiranic compounds[6] or intermediates in the synthesis of fused heterocycles such as benzoselenadiazoles and benzothiadiazoles,[7] benzopyrazoles and benzisoxazoles[8,9] or carbazole derivatives.[10]

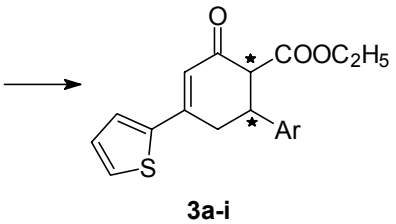
The synthesis of 6-acetyl-5-aryl-2-cyclohexenones or 5-aryl-6-carbethoxy-2-cyclohexenones substituted in position 4 with a 2-thienyl moiety through the Michael addition of acetylacetone and ethyl acetoacetate respectively to 3-aryl-1-(2-thienyl)-2-propenones, as well as these cyclohexenones' involvement in various reactions have been already briefly described.[11] Further on our studies on the preparation[12] and reactivity[13,14] of heterochalcones derived from 2-acetylthiophene, this paper presents the

synthesis of some new 5-aryl-6-carbethoxy-3-(2-thienyl)-2-cyclohexenones, whose various chemical functions commend them as valuable intermediates in subsequent reactions.

Results and discussion

The reaction of chalcones and their heterocyclic analogs with ethyl acetoacetate is known to lead to three structurally diverse types of compounds, depending on the experimental conditions employed: pyrylium salts,[15] Michael addition products[16] and cyclohexenone derivatives.[17] The catalyst plays a key role in directing the reaction to different end products. A strong Lewis acid such as boron trifluoride etherate generates pyrylium cations from the reaction of chalcones and acetoacetic acid esters, but basic catalysts would turn the intermediate Michael addition product into cyclohexenones through the intramolecular cyclocondensation of the methyl group originating from acetoacetic acid ester and the ketone function of the initial chalcone. Thus, in the presence of a base, thienyl-containing chalcone analogs **1** and ethyl acetoacetate **2** produce cyclohexenones **3** by means of an intermediate Michael adduct, as outlined in Scheme 1.





Compound	Ar
3a	3-methoxyphenyl
3b	3,4-dimethoxyphenyl
3c	3,4-methylenedioxyphenyl
3d	3,4,5-trimethoxyphenyl
3e	5-bromo-2-methoxyphenyl
3f	3-bromo-4-methoxyphenyl
3g	4-benzyloxyphenyl
3h	4-benzyloxy-3-methoxyphenyl
3i	2-benzyloxy-5-bromophenyl

Scheme 1. Cyclohexenones **3** through cyclocondensation of chalcone analogs **1** derived from 2-acetylthiophene with ethyl acetoacetate.

The cyclocondensation of ethyl acetoacetate with chalcones **1** leads to the generation of two chiral centers at C^1 and C^6 in the structure of cyclohexenones **3**. As the explored reaction is not stereoselective, both configuration of the chiral carbon atoms are expected to be noticed in the synthesized cyclohexenones **3**, which would result in a mixture of diastereomers. No attempt to separate the diastereomeric cyclohexenones **3** has been undertaken, and the cyclocondensation products have been characterized in the form of the mixture originated from the synthesis.

Literature reveals the involvement of both organic (sodium ethoxide, piperidine, diethylamine) and inorganic (alkaline hydroxides) basic catalysts in this sort of synthesis. In our hands, the use of sodium hydroxide as a catalyst, as described by Hanson,[18] provided the desired cyclohexenones **3** in good yield.

The organic compounds were separated out by pouring the reaction mixture in water. Compound **3b** precipitated as a solid while the other cyclohexenones were initially oily compounds that after being kept for several days turned into solid materials as well. Compound **3g** did not separate as a solid even after three weeks, and the organics were isolated in this case by extracting them in diethyl ether. The slow removal of the solvent at room temperature finally led to a solid material that was recrystallized. The yields of the cyclocondensation are good, varying form 43 to 79%.

Structural analysis of the newly synthesized cyclohexenones **3** comprised IR and NMR investigations. The IR spectra of these compounds revealed a sharp strong absorption band above 1700 cm^{-1} that can be correlated with the presence of the ester function in the structure of cyclohexenones **3**. Furthermore, another sharp strong absorption band was noticed at approximately 1660 cm^{-1} and was assigned to the carbonyl group conjugated with a carbon-carbon double bond. No other absorption band could be evidenced in the region of the IR spectrum associated with the stretching vibrations of the carbonyl group, thus excluding the intermediate Michael adduct having an extra carbonyl group. The ^{1}H-NMR spectra substantiated the results of the IR analysis. The characteristic signals of an ethyl ester moiety (a triplet at chemical shift values of about 1 ppm and a quartet at δ values above 4 ppm) confirmed the presence of the ester group in the structure of cyclohexenones **3**. The proton at C^6 of the cyclohexenone skeleton usually appears as a multiplet immediately below 3 ppm, excepting the case of *ortho*-alkoxyaryl-substituted compounds **3e** and **3i**, when the

signals due to this proton shift to higher δ values and mingle with the peaks attributed to the proton at C^1. The latter proton's signals at about 3.15 ppm turn up as two pairs of doublets, on one hand as a result of the splitting due to the neighbouring C^6 proton and owing to the possible *cis-trans* geometry on the other hand. The two diastereotopic protons at C^5 of the cyclohexenone ring are represented in the ^{1}H NMR spectra of compounds **3** as a multiplet at 3.6-3.8 ppm, again with the exception of **3e** and **3i** whose bulky *ortho*-alkoxyaryl substituent at C^6 causes a change of the typical chemical shift value and leads to the superimposition of these protons' signals over the quartet recorded for the methylene group in the ester function. The characteristic signal in the ^{1}H NMR spectra of compounds **3** is however the singlet of the vinylic proton in the position 3 of the cyclohexenone ring, that occurs at approximately 6.5 ppm and confirms that the intramolecular cyclocondensation subsequent to the Michael addition actually took place. As for the protons in the aromatic region, a similar pattern throughout the ^{1}H NMR spectra of all compounds **3** allowed the assignment of the protons in the thiophene ring at approximately 7.10, 7.40 and 7.48 ppm. The number of the other aromatic protons of the aryl substituent in the position 6 of the cyclohexenone ring that was integrated in the ^{1}H NMR spectra of compounds **3** was always in good agreement with the factual one.

Conclusions

The reaction of several chalcone analogs containing a thiophene ring with ethyl acetoacetate in the presence of catalytic amounts of NaOH has been shown to afford, *via* a Michael addition followed by an intramolecular cyclocondensation, cyclohexenone derivatives which are useful intermediates in the synthesis of structurally diverse heterocycles.

Experimental

Elemental analysis was performed on a Carlo Erba 1106 analyzer. Melting points were taken on a Boëtius melting point microscope and are uncorrected. IR spectra were recorded on a SPECORD M80 spectrometer in KBr pellets. NMR analysis was conducted on a Bruker DXR-500 (500 MHz) instrument in $CDCl_3$. All chemical shifts

are reported in ppm downfield from tetramethylsilane; the coupling constants (*J*) are given in Hz.

The synthesis of chalcones **1** having a 2-thienyl moiety was performed as reported.[12,19-21] All other reagents are commercially available compounds and have been used without prior purification.

General procedure for the synthesis of ethyl esters of 6-aryl-4-(2-thienyl)cyclohex-3-en-2-one-1-carboxylic acids through NaOH-catalyzed cyclocondensation of 3-aryl-1-(2-thienyl)prop-2-enones with ethyl acetoacetate. Thienyl-containing chalcone analog **1** (3 mmol) and ethyl acetoacetate **2** (0.39 g, 0.40 mL, 3 mmol) were refluxed for 2 h in 10-15 mL ethanol in the presence of 0.5 mL 10% NaOH. The reaction mixture was then poured with good stirring into 200 mL ice-cold water and kept at room temperature until the reaction product separated as a solid, which was filtered off and recrystallized from ethanol. Alternatively, compound **3g** was isolated by extracting the emulsion with diethyl ether. The ether phase was separated and dried over anhydrous Na_2SO_4 prior to be subjected to solvent removal. The solid residue obtained was also recrystallized from ethanol.

Ethyl 6-(3-methoxyphenyl)-4-(2-thienyl)cyclohex-3-en-2-one-1-carboxylate (3a). Yellow crystals, (0.65 g, 61%), mp 90-91 °C. Anal. Calcd for $C_{20}H_{20}O_4S$: C 67.39, H 5.66. Found: C 67.52, H 5.51. IR (KBr, cm^{-1}): 1660 ($\nu_{C=O}$ ketone), 1740 ($\nu_{C=O}$ ester). ^1H NMR (500 MHz, $CDCl_3$): δ 1.07 (3H, t, *J* 6.8 Hz, -$CH_2C\underline{H}_3$), 2.92-2.98 (1H, m, >CHAr), 3.15 (1H, dd, J_{trans} 2.9 Hz, J_{cis} 17.4 Hz, >$CHCOOC_2H_5$), 3.73-3.79 (2H, m, -$C\underline{H}_2$CHAr-), 3.82 (3H, s, -OCH_3), 4.08 (2H, q, *J* 6.8 Hz, -$C\underline{H}_2CH_3$), 6.55 (1H, s, =CH-CO-), 6.83 (1H, d, $J_{1,2}$ 7.7 Hz, Ar-H), 6.67 (1H, s, Ar-H), 6.91 (1H, d, $J_{1,2}$ 7.2 Hz), 7.11 (1H, s), 7.28 (1H, t, $J_{1,2}$ 7.2 Hz, $J_{1,2}$ 7.7 Hz, Ar-H), 7.39 (1H, s), 7.48 (1H, d, $J_{1,2}$ 4 Hz).

Ethyl 6-(3,4-dimethoxyphenyl)-4-(2-thienyl)cyclohex-3-en-2-one-1-carboxylate (3b). Yellow crystals, (0.60 g, 52%), mp 126-127 °C. Anal. Calcd for $C_{21}H_{22}O_5S$: C 65.27, H 5.74. Found: C 65.08, H 5.79. IR (KBr, cm^{-1}): 1660 ($\nu_{C=O}$ ketone), 1745 ($\nu_{C=O}$ ester). ^1H NMR (500 MHz, $CDCl_3$): δ 1.08 (3H, t, *J* 6.9 Hz, -$CH_2C\underline{H}_3$), 2.9-2.98 (1H, m, >CHAr), 3.15 (1H, dd, J_{trans} 3 Hz, J_{cis} 17.6 Hz, >$CHCOOC_2H_5$), 3.7-3.77 (2H, m, -$C\underline{H}_2$CHAr-),

3.88 and 3.89 (3H, s, -OCH_3), 4.07 (2H, q, *J* 6.9 Hz, -C$\underline{H}_2CH_3$), 6.54 (1H, s, =CH-CO-), 6.82 (1H, s, Ar-H), 6.85 (1H, d, $J_{1,2}$ 7.9 Hz, Ar-H), 6.88 (1H, d, $J_{1,2}$ 7.9 Hz, Ar-H), 7.11 (1H, t, $J_{1,2}$ 4 Hz), 7.39 (1H, s), 7.49 (1H, d, $J_{1,2}$ 4.7 Hz).

Ethyl 6-(3,4-methylenedioxyphenyl)-4-(2-thienyl)cyclohex-3-en-2-one-1-carboxylate (3c). Yellow crystals, (0.48 g, 43%), mp 123-124 °C. Anal. Calcd for $C_{20}H_{18}O_6S$: C 64.85, H 4.90. Found: C 64.98, H 4.84. IR (KBr, cm^{-1}): 1660 ($\nu_{C=O}$ ketone), 1740 ($\nu_{C=O}$ ester). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.11 (3H, t, *J* 7 Hz, -$CH_2C\underline{H}_3$), 2.84-2.93 (1H, m, >CHAr), 3.12 (1H, dd, J_{trans} 3.8 Hz, J_{cis} 17.8 Hz, >$CHCOOC_2H_5$), 3.61-3.74 (2H, m, -C$\underline{H}_2$CHAr-), 4.09 (2H, q, *J* 7 Hz, -C$\underline{H}_2CH_3$), 5.96 (2H, s, -OCH_2O-), 6.53 (1H, s, =CH-CO-), 6.78 (2H, s, Ar-H), 6.81 (1H, d, Ar-H), 7.10 (1H, t, $J_{1,2}$ 4 Hz), 7.38 (1H, s), 7.48 (1H, d, $J_{1,2}$ 4.7 Hz).

Ethyl 4-(2-thienyl)-6-(3,4,5-trimethoxyphenyl)cyclohex-3-en-2-one-1-carboxylate (3d). Yellow crystals, (0.99 g, 79%), mp 164-165 °C. Anal. Calcd for $C_{22}H_{24}O_6S$: C 63.44, H 5.81. Found: C 63.33, H 5.87. IR (KBr, cm^{-1}): 1660 ($\nu_{C=O}$ ketone), 1740 ($\nu_{C=O}$ ester). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.10 (3H, t, *J* 6.7 Hz, -$CH_2C\underline{H}_3$), 2.89-2.99 (1H, m, >CHAr), 3.17 (1H, dd, J_{trans} 3.5 Hz, J_{cis} 17.7 Hz, >$CHCOOC_2H_5$), 3.71-3.79 (2H, m, -C$\underline{H}_2$CHAr-), 3.84 and 3.86 (3H, s, -OCH_3), 4.10 (2H, q, *J* 6.7 Hz, -C$\underline{H}_2CH_3$), 6.52 (2H, s, Ar-H), 6.55 (1H, s, =CH-CO-), 7.10 (1H, t, $J_{1,2}$ 4 Hz), 7.41 (1H, s); 7.49 (1H, d, $J_{1,2}$ 4.7 Hz).

Ethyl 6-(5-bromo-2-methoxyphenyl)-4-(2-thienyl)cyclohex-3-en-2-one-1-carboxylate (3e). Yellow crystals, (0.89 g, 68%), mp 155-156 °C. Anal. Calcd for $C_{20}H_{19}BrO_4S$: C 55.18, H 4.40. Found: C 55.32, H 4.28. IR (KBr, cm^{-1}): 1670 ($\nu_{C=O}$ ketone), 1730 ($\nu_{C=O}$ ester). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.08 (3H, t, *J* 7 Hz, -$CH_2C\underline{H}_3$), 3.06-3.13 (2H, m, >CHAr and >$CHCOOC_2H_5$), 3.85 (3H, s, -OCH_3), 3.96-4.04 (2H, m, -C$\underline{H}_2$CHAr-), 4.09 (2H, q, *J* Hz, -C$\underline{H}_2CH_3$), 6.53 (1H, s, =CH-CO-), 6.79 (1H, d, $J_{1,2}$ 9 Hz, Ar-H), 7.10 (1H, br s), 7.32 (1H, d, $J_{1,3}$ 2.2 Hz, Ar-H), 7.35 (1H, d, $J_{1,3}$ 2.2 Hz, Ar-H), 7.37-7.40 (2H, m), 7.48 (1H, d, $J_{1,2}$ 5.1 Hz).

Ethyl 6-(3-bromo-4-methoxyphenyl)-4-(2-thienyl)cyclohex-3-en-2-one-1-carboxylate (3f). Yellow crystals, (0.96 g, 74%), mp 130-131 °C. Anal. Calcd for $C_{20}H_{19}BrO_4S$: C 55.18, H 4.40. Found: C 55.03, H 4.46. IR (KBr, cm^{-1}): 1660 ($\nu_{C=O}$ ketone), 1745 ($\nu_{C=O}$ ester). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.11 (3H, t, *J* 6.9 Hz, -$CH_2C\underline{H}_3$), 2.87-2.97 (1H, m, >CHAr), 3.13 (1H, dd, J_{trans} 3.3 Hz, J_{cis} 16.2 Hz, >$CHCOOC_2H_5$), 3.63-3.78 (2H, m, -$C\underline{H}_2$CHAr-), 3.91 (3H, s, -OCH_3), 4.10 (2H, q, *J* 6.9 Hz, -$C\underline{H}_2CH_3$), 6.55 (1H, s, =CH-CO-), 6.89 (1H, d, $J_{1,2}$ 8.1 Hz, Ar-H), 7.12 (1H, br s), 7.25 (1H, d, $J_{1,2}$ 8.1 Hz, Ar-H), 7.40 (1H, s), 7.50 (1H, d, $J_{1,2}$ 4.7 Hz), 7.53 (1H, s).

Ethyl 6-(4-benzyloxyphenyl)-4-(2-thienyl)cyclohex-3-en-2-one-1-carboxylate (3g). Yellow crystals, (0.60 g, 46%), mp 144-145 °C. Anal. Calcd for $C_{26}H_{24}O_4S$: C 72.22, H 5.55. Found: C 71.97, H 5.46. IR (KBr, cm^{-1}): 1660 ($\nu_{C=O}$ ketone), 1745 ($\nu_{C=O}$ ester). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.05 (3H, t, *J* 6.8 Hz, -$CH_2C\underline{H}_3$), 2.86-2.96 (1H, m, >CHAr), 3.13 (1H, dd, J_{trans} 3.3 Hz, J_{cis} 16.3 Hz, >$CHCOOC_2H_5$), 3.64-3.79 (2H, m, -$C\underline{H}_2$CHAr-), 4.05 (2H, q, *J* 6.8 Hz, -$C\underline{H}_2CH_3$), 5.06 (2H, s, -$OC\underline{H}_2C_6H_5$), 6.54 (1H, s, =CH-CO-), 6.96 (1H, d, $J_{1,2}$ 8 Hz, Ar-H), 7.10 (1H, s), 7.24 (1H, d, $J_{1,2}$ 8 Hz, Ar-H), 7.32-7.45 (6H, m), 7.48 (1H, d, $J_{1,2}$ 4.4 Hz).

Ethyl 6-(4-benzyloxy-3-methoxyphenyl)-4-(2-thienyl)cyclohex-3-en-2-one-1-carboxylate (3h). Yellow crystals, (0.86 g, 62%), mp 139-140 °C. Anal. Calcd for $C_{27}H_{26}O_5S$: C 70.11, H 5.67. Found: C 70.23, H 5.59. IR (KBr, cm^{-1}): 1650 ($\nu_{C=O}$ ketone), 1730 ($\nu_{C=O}$ ester). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.06 (3H, t, *J* 6.9 Hz, -$CH_2C\underline{H}_3$), 2.86-2.97 (1H, m, >CHAr), 3.14 (1H, dd, J_{trans} 3 Hz, J_{cis} 17.6 Hz, >$CHCOOC_2H_5$), 3.64-3.78 (2H, m, -$C\underline{H}_2$CHAr-), 3.90 (3H, s, -OCH_3), 4.06 (2H, q, *J* 6.9 Hz, -$C\underline{H}_2CH_3$), 5.15 (2H, s, -$OC\underline{H}_2C_6H_5$), 6.54 (1H, s, =CH-CO-), 6.80 (1H, d, $J_{1,2}$ 7.9 Hz), 6.82-6.89 (2H, m, Ar-H), 7.10 (1H, br s), 7.28-7.33 (1H, m), 7.34-7.41 (3H, m), 7.42-7.46 (2H, m), 7.48 (1H, d, $J_{1,2}$ 4.4 Hz).

Ethyl 6-(2-benzyloxy-5-bromophenyl)-4-(2-thienyl)cyclohex-3-en-2-one-1-carboxylate (3i). Yellow crystals, (1.03 g, 67%), mp 134-135 °C. Anal. Calcd for $C_{26}H_{23}BrO_4S$: C 61.06, H 4.53. Found: C 60.90, H 4.59. IR (KBr, cm^{-1}): 1660 ($\nu_{C=O}$ ketone), 1740 ($\nu_{C=O}$ ester). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.10 (3H, t, *J* 6.9 Hz, -$CH_2C\underline{H}_3$), 3.01-3.15 (2H,

m, >CHAr and >CHCOOC$_2$H$_5$), 4.01-4.17 (4H, m, -C<u>H$_2$</u>CHAr- and -C<u>H$_2$</u>CH$_3$), 5.13 (2H, s, -OC<u>H$_2$</u>C$_6$H$_5$), 6.50 (1H, s, =CH-CO-), 6.84 (1H, d, $J_{1,2}$ 8.6 Hz, Ar-H), 7.09 (1H, br s), 7.28-7.36 (6H, m), 7.38-7.43 (2H, m), 7.47 (1H, d, $J_{1,2}$ 4.2 Hz).

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Povzetek

S pomočjo NaOH katalizirane ciklokondenzacije 3-aril-1-(2-tienil)prop-2-en-1-onov z etil acetoacetatom smo pripravili devet novih 6-aril-4-(2-tienil)cikloheks-3-en-2-on-1-karboksilatov, uporabnih intermediatov v sintezi prikondenziranih heterociklov.