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A CONVENIENT SYNTHESIS OF 2-AMINO-5,6,7,8,-TETRAHYDRO-5-OXO-4-ARYL-7,7-DIMETHYL-4H-BENZO-[b]-PYRAN-3-ETHYLCARBOXYLATES UNDER MICROWAVE IRRADIATION

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SYNTHETIC COMMUNICATIONS, 31(17), 2663–2666 (2001)

A CONVENIENT SYNTHESIS OF 2-AMINO-5,6,7,8,-TETRAHYDRO-5-OXO-4-ARYL-7,7-DIMETHYL-4*H*-BENZO-[b]-PYRAN-3-ETHYLCARBOXYLATES UNDER MICROWAVE IRRADIATION

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ABSTRACT

A series of 2-amino-5,6,7,8-tetrahydro-5-oxo-4-aryl-7,7-dimethyl-4*H*-benzo-[b]-pyran-3-ethylcarboxylates were synthesized by reaction of β -cyano- β -carbothoxy styrene and 5,5-dimethyl-1,3-cyclo-hexanedione under microwave irradiation without catalyst and solvent.

Microwave heating and its application in organic synthesis has been reviewed recently.¹ Rate enhancement in many reactions has been reported.² We have been working on developing new synthetic methods for the preparation of substituted 4H-benzo-[b]-pyrans employing both microwave irradiation and dry reaction conditions.

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The title compound is a useful and versatile building block for the synthesis of a number of unusual natural products.³ Their conventional syntheses involve acid as well as base catalyzed condensation of appropriate active methylene carbonyl compounds and are plagued by prolonged reaction times, poor yields, and side reactions of the aldehydes. Kamaljit S. et al. reported⁴ that 2-amino-5,6,7,8-tetrahydro-5-oxo-4-aryl-7,7-dimethyl-4*H*-benzo-[b]-pyran-3-ethylcarboxylates(3) were synthesized from β -cyano- β -carbethoxy styrene and 1,3-cyclohexanedione in refluxing acetonitrile: acetic acid (10:1). Here we would like to report a convenient synthesis of these compounds using reaction condition which employ microwave irradiation without catalyst and solvent. The reactions are completed in 4–8 min with yields of 61–90%.



The results are shown in the Table 1.

EXPERIMENTAL

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a Nicolet FI-IR50DX instrument. ¹HNMR spectra were measured on a DPX 300 MHz spectrometer using TMS as internal standard. Elemental analyses were determined by using Perkin-Elmer 240c elemental analysis. Microwave irradiation was carried

Entry	Ar	Time (min)	Isolated Yield (%)
3a	C ₆ H ₅	4	61
3b	$2-ClC_6H_4$	7	90
3c	$4-ClC_6H_4$	6	74
3d	$3,4-OCH_2OC_6H_3$	8	61
3e	3,4-(OCH ₃) ₂ C ₆ H ₃	8	87
3f	$3-NO_2C_6H_4$	7	81
3g	$4-BrC_6H_4$	6	77

Table 1.	Syntheses of	Compound 3	Under	Microwave	Irradiation
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MICROWAVE IRRADIATION

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out with a commercial microwave oven (2450 MHz, 500 W) under atmospheric pressure.

General Procedure

 β -Cyano- β -carbethoxy styrene was synthesized from aromatic aldehydes and ethyl cyanoacetate with KF-alumina as catalyst refluxing in alcohol. Other reagents were used without further purification.

5,5-Dimethyl-1,3-cyclohexanedione (5 mmol) and β -amino- β -carbethoxy styrene (5 mmol) were thoroughly mixed with silica (2 g) in an agate mortar. The resulting fine power was transferred to a flask (50 mL) connected with refluxing equipment. After irradiation of several minutes, the reaction mixture was cooled to room temperature. The crude products were purified by recrystallization from 95% EtOH or column chromatography to give (3).

3a: m.p. 146–148°C. IR (KBr, v, cm⁻¹): 3400, 3300, 1700, 1654. ¹HNMR (CDCl₃): δ 0.98 (s, 3H, CH₃), 1.10 (s, 3H, CH₃), 1.15 (t, J = 7.11 Hz, 3H, CH₃), 2.18 (m, 2H, CH₂), 2.44 (s, 2H, CH₂), 4.02 (q, J = 7.01 Hz, 2H, CH₂), 4.71 (s, 1H, CH), 6.20 (brs, 2H, NH₂), 7.26–7.45 (m, 5H, ArH); Anal. calcd. (%) for C₂₀H₂₃NO₄, C 70.38, H 6.74, N 4.10; found: C 70.16, H 6.88, N 4.03.

3b: m.p. 166–168°C. IR (KBr, *v*, cm⁻¹): 3400, 3300, 1680, 1654. ¹HNMR (CDCl₃): δ 0.99 (s, 3H, CH₃), 1.08 (s, 3H, CH₃), 1.12 (t, J=7.11 Hz, 3H, CH₃), 2.19 (m, 2H, CH₂), 2.41 (s, 2H, CH₂), 4.01 (q, J=7.12 Hz, 2H, CH₂), 5.00 (s, 1H, CH), 6.27 (brs, 2H, NH₂), 7.04–7.32 (m, 4H, ArH); Anal. calcd. (%) for C₂₀H₂₂ClNO₄, C 63.91, H 5.90, N 3.72; found: C 63.80, H 6.12, N 3.83.

3c: m.p. 149–150°C. IR (KBr, *v*, cm⁻¹): 3438, 3304, 1680, 1658. ¹HNMR (CDCl₃): δ 0.98 (s, 3H, CH₃), 1.08 (s, 3H, CH₃), 1.14 (t, J=7.11 Hz, 3H, CH₃), 2.14 (m, 2H, CH₂), 2.43 (s, 2H, CH₂), 4.06 (q, J=7.11 Hz, 2H, CH₂), 4.68 (s, 1H, CH), 6.21 (brs, 2H, NH₂), 7.16–7.30 (m, 4H, ArH); Anal. calcd. (%) for C₂₀H₂₂ClNO₄, C 63.91, H 5.90, N 3.72; found: C 63.79, H 6.10, N 3.90.

3d: m.p. 142–144°C. IR (KBr, v, cm⁻¹): 3402, 3300, 1683, 1657. ¹HNMR (CDCl₃): δ 1.00 (s, 3H, CH₃), 1.10 (s, 3H, CH₃), 1.17 (t, J = 7.14 Hz, 3H, CH₃), 2.18 (m, 2H, CH₂), 2.43 (s, 2H, CH₂), 4.08 (q, J = 7.14 Hz, 2H, CH₂), 4.64 (s, 1H, CH), 5.93 (s, 2H, OCHO), 6.17 (brs, 2H, NH₂), 6.71–6.76 (m, 3H, ArH); Anal. calcd. (%) for C₂₁H₂₃NO₆, C 65.44, H 6.01, N 3.63; found: C 65.32, H 5.92, N 3.78.

3e: m.p. 155–157°C. IR (KBr, v, cm⁻¹): 3448, 3346, 1698, 1662. ¹HNMR (CDCl₃): δ 0.98 (s, 3H, CH₃), 1.09 (s, 3H, CH₃), 1.18 (t, J = 7.11 Hz, 3H,



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CH₃), 2.19 (m, 2H, CH₂), 2.41 (s, 2H, CH₂), 3.81 (s, 3H, OCH₃) 3.85 (s, 3H, OCH₃), 4.05 (q, J = 7.08 Hz, 2H, CH₂), 4.65 (s, 1H, CH), 6.21 (brs, 2H, NH₂), 6.70–6.86 (m, 3H, ArH); Anal. calcd. (%) for $C_{22}H_{27}NO_6$, C 65.82, H 6.78, N 3.49; found: C 65.93, H 6.70, N 3.50.

3f: m.p. 172–174°C. IR (KBr, v, cm⁻¹): 3500, 3310, 1698, 1679. ¹HNMR (CDCl₃): δ 0.98 (s, 3H, CH₃), 1.11 (s, 3H, CH₃), 1.15 (t, J = 7.11 Hz, 3H, CH₃), 2.18 (m, 2H, CH₂), 2.47 (s, 2H, CH₂), 4.04 (q, J = 7.14 Hz, 2H, CH₂), 4.79 (s, 1H, CH), 6.33 (brs, 2H, NH₂), 7.35–8.10 (m, 4H, ArH); Anal. calcd. (%) for C₂₀H₂₂N₂O₆, C 62.16, H 5.74, N 7.25; found: C 62.07, H 5.90, N 7.38.

3g: m.p. 160–162°C. IR (KBr, v, cm⁻¹): 3448, 3310, 1684, 1647. ¹HNMR (CDCl₃): δ 0.99 (s, 3H, CH₃), 1.10 (s, 3H, CH₃), 1.16 (t, J = 7.11 Hz, 3H, CH₃), 2.18 (m, 2H, CH₂), 2.42 (s, 2H, CH₂), 4.05 (q, J = 7.13 Hz, 2H, CH₂), 4.66 (s, 1H, CH), 6.23 (brs, 2H, NH₂), 7.13–7.34 (m, 4H, ArH); Anal. calcd. (%) for C₂₀H₂₂BrNO₄, C 57.15, H 5.27, N 3.33, found: C 57.00, H 5.38, N 3.43.

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