

DABCO CATALYZED SYNTHESIS OF NEW 2-AMINO-8-ARYLIDENE-4-ARYL-5,6,7,8-TETRAHYDROBENZO-4H-PYRAN-3-CARBONITRILES FROM α,α' -BIS(SUBSTITUTED BENZYLIDENE)CYCLOALKANONES

Gholam Hossein Mahdavinia^{1*}, Mohammad Ali Bigdeli² and Fatemeh Kooti²

¹Department of Chemistry, Marvdasht Branch, Islamic Azad University, Marvdasht, Iran

²Faculty of Chemistry, Tarbiat Moallem University, 49 Mofateh St., Tehran, Iran

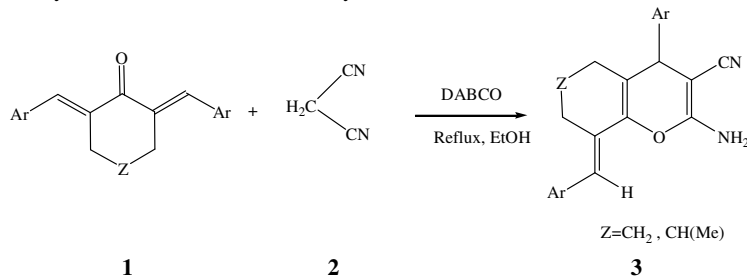
(Received June 2, 2011; revised January 10, 2012)

ABSTRACT. The synthesis of new series of 2-amino-8-arylidene-4-aryl-5,6,7,8-tetrahydrobenzo-4H-pyran-3-carbonitriles from the reaction of α,α' -bis(substituted benzylidene)cycloalkanones with malononitrile under reflux conditions in the presence DABCO in good to excellent yields has been described.

KEY WORDS: DABCO, 4H-Pyran, α,α' -bis(substituted benzylidene)cycloalkane

INTRODUCTION

4H-pyran and its derivatives are important class of organic and bioorganic compounds. They are often used in cosmetics, pigments and are utilized as potentially biodegradable agrochemicals [1, 2]. A number of compounds containing 4H-pyrane moiety have been used in wide range of therapeutic areas [3-5]. Polyfunctionalized 4H-pyrans constitute a structural unit of a number of biologically interesting compounds which possess various pharmacological activities, such as antiallergic [5], antitumor [6] and antibacterial [7-8]. 4H-Pyran derivatives are also potential calcium channel antagonists [9] which are structurally similar to biologically active 1,4-dihydropyridines. In addition, 2-amino-4H-benzo[b]pyrans are used in the synthesis of difficultly accessible annulated heterocyclic [10].



Scheme 1. Synthesis of 2-amino-8-arylidene-4-aryl-5,6,7,8-tetrahydrobenzo-4H-pyran-3-carbonitrile.

The 4H-pyrans are synthesized mainly by a three-component coupling reaction of aromatic aldehydes and malononitrile with ketones or β -diketones by bases catalysts or acid catalysts. Many of the methods reported for the synthesis of these compounds in the literature [11-28]. Recently synthesis and biological properties of the new series of this compound entitled 2-amino-8-arylidene-4-aryl-5,6,7,8-tetrahydrobenzo-4H-pyran-3-carbonitriles have been attracted

*Corresponding author. E-mail: hmahdavinia@gmail.com

for chemist [29-31]. For the mentioned reasons and as part of our study on the development of new routes to the synthesis of heterocyclic system [32], in this paper, we report the synthesis of some new 2-amino-8-arylidene-4-aryl-5,6,7,8-tetrahydrobenzo-4H-pyran-3-carbonitrile from α,α -bis(substituted benzylidene)cycloalkanones and malononitrile in ethanol in the presence of DABCO under reflux conditions (Scheme 1).

EXPERIMENTAL

Chemicals were purchased from Fluka and Merck. Melting points were determined using an Electrothermal 9100 and are not corrected for known compounds. Thin layer chromatography (TLC), on commercial aluminum-backed plates of silica gel 60PF254, was used to monitor the progress of the reactions. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance-300 MHz spectrometer in the presence of TMS as internal standard. IR spectra were recorded using a Perkin-Elmer 843 spectrometer using KBr discs.

General procedure for 2-amino-3-cyano-4H-pyran derivatives

A mixture of the bisarylidene cyclohexanone **1** (1 mmol), malononitrile **2** (1 mmol), and DABCO (10 mol %) in ethanol (15 mL) was stirred at reflux condition for appropriate time according to Table 1. After completion of the reaction, the mixture was kept at room temperature and the resulting crystalline product was collected by filtration and it was washed with cold ethanol. The product was found to be pure and no further purification was necessary.

Table 1. Synthesis of 2-amino-8-arylidene-4-aryl-5,6,7,8-tetrahydrobenzo-4H-pyran-3-carbonitrile.

Product	Ar	Z	Time (min)	Yield ^a (%)	M.p. ($^{\circ}\text{C}$)	
					Found	Reported
3a	C ₆ H ₅	CH ₂	5	95	232-234	230-231 [29]
3b	4-MeC ₆ H ₄	CH ₂	15	90	165-166	161-162 [29]
3c	4-ClC ₆ H ₄	CH ₂	20	95	220-221	215-216 [29]
3d	2-ClC ₆ H ₄	CH ₂	10	90	238-240	237-238 [29]
3e	4-MeOC ₆ H ₄	CH ₂	15	80	221-223	-----
3f	4-FC ₆ H ₅	CH ₂	20	95	227-230	-----
3g	4-BrC ₆ H ₄	CH ₂	20	90	219-221	-----
3h	C ₆ H ₅	CH(Me)	15	80	205-208	-----
3i	4-MeC ₆ H ₄	CH(Me)	20	80	218-221	-----
3j	4-MeOC ₆ H ₄	CH(Me)	25	80	200-203	-----
3k	4-ClC ₆ H ₄	CH(Me)	15	85	201-204	-----
3l	4-FC ₆ H ₄	CH(Me)	20	90	207-209	-----
3m	2-ClC ₆ H ₄	CH(Me)	25	90	137-140	-----
3n	4-BrC ₆ H ₄	CH(Me)	15	80	230-232	-----

^aIsolated yields.

2-Amino-8-[4-methoxybenzylidene]-4-(4-methoxyphenyl)-5,6,7,8-tetrahydrobenzo-4H-pyran-3-carbonitrile. IR (KBr): ν_{max} = 3477, 3377, 2196, 1673, 1640, 1609, 1515, 1412, 1255 cm^{-1} . Anal. calcd (%) for C₂₅H₂₄N₂O₃: C, 75.01; H, 6.01; N, 7.01; found: C, 74.26; H, 6.04; N, 6.90. ^1H NMR (300 MHz, CDCl₃): δ = 1.54-2.05 (m, 4H, 2 CH₂), 2.53-2.76 (m, 2H, CH₂), 3.80 (s, 3H, MeO), 3.83 (s, 3H, MeO), 3.92 (s, 1H, CH), 4.48 (s, 2H, NH₂), 6.81 (s, 1H, CH=C), 6.85-7.28 (m, 8H, 2 C₆H₄). ^{13}C NMR (75 MHz, CDCl₃): δ = 22.3, 27.1, 27.4, 42.7, 55.3, 60.8, 113.6, 114.1, 114.7, 122.0, 127.9, 128.9, 129.5, 130.5, 135.1, 141.4, 145.0, 158.4, 158.7, 158.8. MS (EI, 70 eV): m/z = 400.22 [M⁺].

2-Amino-8-[4-fluorobenzylidene]-4-(4-fluorophenyl)-5,6,7,8-tetrahydrobenzo-4H-pyran-3-carbonitrile (3e). IR (KBr): ν_{\max} = 3470, 3329, 2198, 1674, 1645, 1506, 1416, 1224 cm^{-1} . Anal. calcd (%) for $\text{C}_{23}\text{H}_{18}\text{F}_2\text{N}_2\text{O}$: C, 73.40; H, 4.78; N, 7.45; found: C, 73.31; H, 4.72; N, 7.45. ^1H NMR (300 MHz, CDCl_3): δ = 1.54-1.70 (m, 2H, CH_2), 1.87-2.06 (m, 2H, CH_2), 2.50-2.73 (m, 2H, CH_2), 3.96 (s, 1H, CH), 4.56 (s, 2H, NH_2), 6.83 (s, 1H, $\text{CH}=\text{C}$), 7.00-7.28 (m, 8H, 2 C_6H_4). ^{13}C NMR (75 MHz, CDCl_3): δ = 22.1, 26.9, 27.3, 42.8, 60.4, 115.0, 115.3, 115.5, 121.7, 129.1, 129.3, 129.4, 130.7, 138.6, 141.8, 158.7, 158.8, 163.4, 163.7.

2-Amino-8-[4-bromobenzylidene]-4-(4-bromophenyl)-5,6,7,8-tetrahydrobenzo-4H-pyran-3-carbonitrile (3f). IR (KBr): ν_{\max} = 3448, 3331, 2197, 1667, 1637, 1599, 1486, 1419 cm^{-1} . Anal. calcd (%) for $\text{C}_{23}\text{H}_{18}\text{Br}_2\text{N}_2\text{O}$: C, 55.42; H, 3.61; N, 5.62; found: C, 55.17; H, 3.31; N, 5.62. ^1H NMR (300 MHz, CDCl_3): δ = 1.60-1.68 (m, 2H, CH_2), 1.86-2.04 (m, 2H, CH_2), 2.51-2.70 (m, 2H, CH_2), 3.94 (s, 1H, CH), 4.56 (s, 2H, NH_2), 6.79 (s, 1H, $\text{CH}=\text{C}$), 7.11-7.49 (m, 8H, 2 C_6H_4). ^{13}C NMR (75 MHz, CDCl_3): δ = 22.1, 27.0, 27.4, 43.1, 60.0, 115.2, 119.7, 120.8, 121.3, 121.7, 129.6, 129.8, 130.8, 131.4, 131.9, 135.7, 141.5, 141.8, 158.8.

2-Amino-8-benzylidene-6-methyl-4-phenyl-5,6,7,8-tetrahydrobenzo-4H-pyran-3-carbonitrile (3g). IR (KBr): ν_{\max} = 3431, 3338, 2185, 1666, 1639, 1619, 1591, 1412 cm^{-1} . Anal. calcd (%) for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}$: C, 81.81; H, 6.01; N, 7.95; found: C, 80.60; H, 6.24; N, 7.84. Major isomer-**3h** (55%); ^1H NMR (300 MHz, CDCl_3): δ = 0.94 (d, J = 6.32 Hz, 3H, Me), 1.68-2.30 (m, 4H, 2 CH_2), 2.87 (m, 1H, CH), 3.98 (s, 1H, CH), 4.52 (s, 2H, NH_2), 6.93 (s, 1H, $\text{CH}=\text{C}$), 7.27-7.42 (m, 8H, 2 C_6H_4). ^{13}C NMR (75 MHz, CDCl_3): δ = 20.9, 28.9, 35.1, 36.1, 43.9, 60.6, 114.6, 120.0, 122.8, 126.8, 127.4, 127.8, 128.8, 129.2, 129.5, 137.0, 141.6, 143.0, 145.0, 158.8. Minor isomer-**3h** (45%); ^1H NMR (300 MHz, CDCl_3): δ = 0.93 (d, J = 6.10 Hz, 3H, Me), 1.68-2.30 (m, 4H, 2 CH_2), 2.90 (m, 1H, CH), 4.00 (s, 1H, CH), 4.56 (s, 2H, NH_2), 6.93 (s, 1H, $\text{CH}=\text{C}$), 7.27-7.42 (m, 8H, 2 C_6H_4). ^{13}C NMR (75 MHz, CDCl_3): δ = 20.9, 28.5, 34.7, 35.1, 43.1, 60.7, 114.5, 120.0, 122.7, 126.8, 127.4, 127.9, 128.7, 129.3, 129.5, 137.0, 141.2, 142.6, 145.0, 158.9.

2-Amino-8-[4-methylbenzylidene]-6-methyl-4-(4-methylphenyl)-5,6,7,8-tetrahydrobenzo-4H-pyran-3-carbonitrile (3h). IR (KBr): ν_{\max} = 3455, 3324, 2203, 1676, 1647, 1602, 1514, 1414 cm^{-1} . Anal. calcd (%) for $\text{C}_{26}\text{H}_{26}\text{N}_2\text{O}$: C, 81.67; H, 6.81; N, 7.32; found: C, 81.40; H, 6.95; N, 7.28. Major isomer-**3i** (55%); ^1H NMR (300 MHz, CDCl_3): δ = 0.88 (d, J = 6.22 Hz, 3H, Me), 1.63-2.26 (m, 4H, 2 CH_2), 3.35 (s, 3H, Me), 2.38 (s, 3H, Me), 2.84 (m, 1H, CH), 3.92 (s, 1H, CH), 4.55 (s, 2H, NH_2), 6.85 (s, 1H, $\text{CH}=\text{C}$), 7.10-7.40 (m, 8H, 2 C_6H_4); ^{13}C NMR (75 MHz, CDCl_3): δ = 21.0, 21.1, 21.2, 28.9, 35.2, 36.0, 43.4, 60.5, 114.2, 120.0, 122.4, 127.8, 128.8, 129.1, 129.3, 133.8, 134.0, 136.5, 136.9, 139.6, 141.1, 158.9. Minor isomer-**3i** (45%); ^1H NMR (300 MHz, CDCl_3): δ = 0.91 (d, J = 6.02 Hz, 3H, Me), 1.63-2.26 (m, 4H, 2 CH_2), 3.34 (s, 3H, Me), 2.37 (s, 3H, Me), 2.88 (m, 1H, CH), 3.90 (s, 1H, CH), 4.52 (s, 2H, NH_2), 6.85 (s, 1H, $\text{CH}=\text{C}$), 7.10-7.40 (m, 8H, 2 C_6H_4); ^{13}C NMR (75 MHz, CDCl_3): δ = 21.0, 21.1, 21.2, 28.5, 34.6, 35.1, 42.6, 60.6, 114.3, 120.1, 122.5, 127.7, 128.6, 129.2, 129.4, 133.8, 134.0, 136.5, 136.8, 140.1, 141.5, 158.9.

2-Amino-8-[4-methoxybenzylidene]-6-methyl-4-(4-methoxyphenyl)-5,6,7,8-tetrahydrobenzo-4H-pyran-3-carbonitrile (3i). IR (KBr): ν_{\max} = 3420, 3328, 2196, 1676, 1647, 1604, 1511, 1417, 1252 cm^{-1} . Anal. calcd (%) for $\text{C}_{26}\text{H}_{26}\text{N}_2\text{O}_3$: C, 75.36; H, 6.28; N, 6.76; found: C, 75.09; H, 6.29; N, 6.72. Major isomer-**3j** (56%); ^1H NMR (300 MHz, CDCl_3): δ = 0.88 (d, J = 6.24 Hz, 3H, Me), 1.61-2.25 (m, 4H, 2 CH_2), 2.82 (m, 1H, CH), 3.80 (s, 3H, MeO), 3.83 (s, 3H, MeO), 3.91 (s, 1H, CH), 4.56 (s, 2H, NH_2), 6.82 (s, 1H, $\text{CH}=\text{C}$), 6.84-7.29 (m, 8H, 2 C_6H_4); ^{13}C NMR (75 MHz, CDCl_3): δ = 21.0, 28.9, 35.2, 36.0, 43.1, 55.1, 55.2, 60.6, 113.6, 113.7, 113.9, 120.1, 122.1, 127.8, 128.9, 129.5, 130.5, 134.9, 141.1, 158.4, 158.7, 158.9. Minor isomer-**3j** (44%);

^1H NMR (300 MHz, CDCl_3): δ = 0.91 (d, J = 6.01 Hz, 3H, Me), 1.61-2.25 (m, 4H, 2 CH_2), 2.87 (m, 1H, CH), 3.79 (s, 3H, MeO), 3.81 (s, 3H, MeO), 3.89 (s, 1H, CH), 4.53 (s, 2H, NH_2), 6.81 (s, 1H, $\text{CH}=\text{C}$), 6.84-7.29 (m, 8H, 2 C_6H_4); ^{13}C NMR (75 MHz, CDCl_3): δ = 21.1, 28.5, 34.6, 35.9, 42.2, 55.1, 55.2, 60.7, 113.7, 114.0, 114.1, 120.1, 122.2, 128.0, 129.6, 130.0, 130.5, 135.3, 141.5, 158.4, 158.7, 158.9.

2-Amino-8-[4-chlorobenzylidene]-6-methyl-4-(4-chlorophenyl)-5,6,7,8-tetrahydrobenzo-4H-pyran-3-carbonitrile (3j). IR (KBr): ν_{max} = 3460, 3318, 2186, 1668, 1632, 1597, 1489, 1415, 1255 cm^{-1} . Anal. calcd (%) for $\text{C}_{24}\text{H}_{20}\text{Cl}_2\text{N}_2\text{O}$: C, 68.08; H, 4.72; N, 6.62; found: C, 68.03; H, 4.52; N, 6.64. Major isomer-**3k** (54%); ^1H NMR (300 MHz, CDCl_3): δ = 0.88 (d, J = 6.25 Hz, 3H, Me), 1.58-2.24 (m, 4H, 2 CH_2), 2.75 (m, 1H, CH), 3.94 (s, 1H, CH), 4.56 (s, 2H, NH_2), 6.82 (s, 1H, $\text{CH}=\text{C}$), 7.15-7.34 (m, 8H, 2 C_6H_4), ^{13}C NMR (75 MHz, CDCl_3): δ = 20.8, 28.8, 35.1, 35.9, 43.4, 60.2, 114.3, 119.5, 121.8, 128.4, 129.0, 129.2, 129.8, 130.5, 132.7, 133.3, 135.3, 141.1, 141.5, 158.8. Minor isomer-**3k** (46%); ^1H NMR (300 MHz, CDCl_3): δ = 0.91 (d, J = 6.03 Hz, 3H, Me), 1.58-2.24 (m, 4H, 2 CH_2), 2.80 (m, 1H, CH), 3.92 (s, 1H, CH), 4.54 (s, 2H, NH_2), 6.82 (s, 1H, $\text{CH}=\text{C}$), 7.15-7.34 (m, 8H, 2 C_6H_4), ^{13}C NMR (75 MHz, CDCl_3): δ = 20.8, 28.5, 34.6, 35.0, 42.6, 60.3, 114.4, 119.5, 122.1, 128.4, 128.9, 129.2, 129.6, 130.5, 132.7, 133.2, 135.3, 141.2, 141.6, 158.9.

2-Amino-8-[4-fluorobenzylidene]-6-methyl-4-(4-fluorophenyl)-5,6,7,8-tetrahydrobenzo-4H-pyran-3-carbonitrile (3k). IR (KBr): ν_{max} = 3475, 3330, 2193, 1673, 1635, 1601, 1506, 1418 cm^{-1} . Anal. calcd (%) for $\text{C}_{24}\text{H}_{20}\text{F}_2\text{N}_2\text{O}$: C, 73.84; H, 5.12; N, 7.18; found: C, 72.23; H, 5.85; N, 7.51. Major isomer-**3l** (56%); ^1H NMR (300 MHz, CDCl_3): δ = 0.88 (d, J = 6.23 Hz, 3H, Me), 1.61-2.24 (m, 4H, 2 CH_2), 2.78 (m, 1H, CH), 3.94 (s, 1H, CH), 4.52 (s, 2H, NH_2), 6.83 (s, 1H, $\text{CH}=\text{C}$), 7.00-7.28 (m, 8H, 2 C_6H_4), ^{13}C NMR (75 MHz, CDCl_3): δ = 20.9, 28.5, 34.6, 35.9, 44.4, 60.6, 114.4, 115.4, 115.8, 119.7, 122.0, 129.1, 129.4, 130.8, 132.9, 138.7, 141.5, 158.8, 160.5, 163.7. Minor isomer-**3l** (44%); ^1H NMR (300 MHz, CDCl_3): δ = 0.91 (d, J = 6.01 Hz, 3H, Me), 1.61-2.24 (m, 4H, 2 CH_2), 2.88 (m, 1H, CH), 3.95 (s, 1H, CH), 4.52 (s, 2H, NH_2), 6.83 (s, 1H, $\text{CH}=\text{C}$), 7.00-7.28 (m, 8H, 2 C_6H_4), ^{13}C NMR (75 MHz, CDCl_3): δ = 20.9, 28.5, 34.6, 35.9, 44.4, 60.6, 114.3, 115.1, 115.6, 119.7, 121.8, 129.1, 129.5, 130.7, 132.9, 138.7, 141.4, 158.7, 160.0, 163.2.

2-Amino-8-[2-chlorobenzylidene]-6-methyl-4-(2-chlorophenyl)-5,6,7,8-tetrahydrobenzo-4H-pyran-3-carbonitrile (3l). IR (KBr): ν_{max} = 3444, 3327, 2195, 1677, 1605, 1470, 1413, 1254 cm^{-1} . Anal. calcd (%) for $\text{C}_{24}\text{H}_{20}\text{Cl}_2\text{N}_2\text{O}$: C, 68.08; H, 4.72; N, 6.62; found: C, 68.02; H, 4.76; N, 6.64. Major isomer-**3m** (56%); ^1H NMR (300 MHz, CDCl_3): δ = 0.88 (d, J = 6.23 Hz, 3H, Me), 1.57-2.29 (m, 4H, 2 CH_2), 2.64 (m, 1H, CH), 3.34 (s, 1H, CH), 4.57 (s, 2H, NH_2), 6.86 (s, 1H, $\text{CH}=\text{C}$), 7.19-7.42 (m, 8H, 2 C_6H_4), ^{13}C NMR (75 MHz, CDCl_3): δ = 20.8, 28.4, 34.5, 35.1, 39.6, 59.2, 114.5, 119.5, 120.2, 127.6, 128.2, 128.5, 129.4, 129.7, 130.4, 130.5, 130.6, 135.2, 139.8, 140.7, 142.3, 145.5, 160.0. Minor isomer-**3m** (44%); ^1H NMR (300 MHz, CDCl_3): δ = 0.91 (d, J = 6.02 Hz, 3H, Me), 1.57-2.29 (m, 4H, 2 CH_2), 2.70 (m, 1H, CH), 3.32 (s, 1H, CH), 4.55 (s, 2H, NH_2), 6.86 (s, 1H, $\text{CH}=\text{C}$), 7.19-7.42 (m, 8H, 2 C_6H_4), ^{13}C NMR (75 MHz, CDCl_3): δ = 20.8, 28.7, 34.4, 35.0, 39.0, 59.3, 114.6, 119.5, 120.1, 127.5, 128.1, 128.3, 129.2, 129.6, 130.5, 130.4, 130.4, 135.4, 139.9, 140.5, 142.1, 145.5, 160.1.

2-Amino-8-[4-bromobenzylidene]-6-methyl-4-(4-bromophenyl)-5,6,7,8-tetrahydrobenzo-4H-pyran-3-carbonitrile (3m). IR (KBr): ν_{max} = 3453, 3316, 2182, 1668, 1594, 1485, 1413 cm^{-1} . Anal. calcd. (%) for $\text{C}_{24}\text{H}_{20}\text{Br}_2\text{N}_2\text{O}$: C, 56.25; H, 3.90; N, 5.47; found: C, 56.26; H, 3.78; N, 5.58. Major isomer-**3n** (56%); ^1H NMR (300 MHz, CDCl_3): δ = 0.89 (d, J = 6.22 Hz, 3H, Me), 1.56-2.24 (m, 4H, 2 CH_2), 2.78 (m, 1H, CH), 3.96 (s, 1H, CH), 4.56 (s, 2H, NH_2), 6.81 (s, 1H,

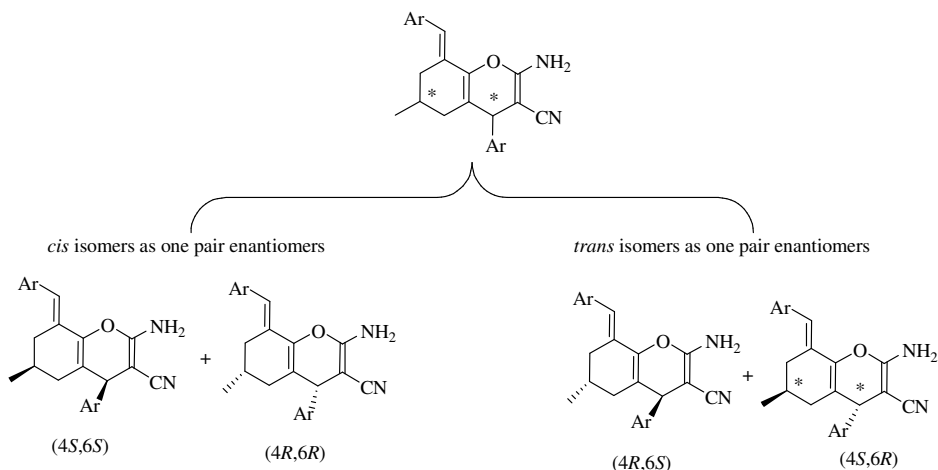
CH=C), 7.21-7.38 (m, 8H, 2 C₆H₄), ¹³C NMR (75 MHz, CDCl₃): δ = 21.0, 28.8, 35.2, 35.9, 43.5, 60.2, 114.4, 120.0, 122.1, 128.4, 129.0, 129.2, 129.8, 130.5, 132.7, 133.3, 135.3, 141.1, 141.5, 158.8. Minor isomer-**3n** (44%); ¹H NMR (300 MHz, CDCl₃): δ = 0.92 (d, *J* = 6.02 Hz, 3H, Me), 1.56-2.24 (m, 4H, 2 CH₂), 2.81 (m, 1H, CH), 3.98 (s, 1H, CH), 4.54 (s, 2H, NH₂), 6.81 (s, 1H, CH=C), 7.21-7.38 (m, 8H, 2 C₆H₄), ¹³C NMR (75 MHz, CDCl₃): δ = 21.0, 28.5, 34.6, 35.0, 42.8, 60.3, 114.5, 120.0, 122.1, 128.4, 128.9, 129.2, 129.6, 130.5, 132.7, 133.2, 135.3, 141.2, 141.6, 158.9.

RESULTS AND DISCUSSION

In a typical experimental procedure, a solution of bisbenzylidenecyclohexanone **1a** and malononitrile **2** in ethanol for synthesis of 2-amino-8-arylidene-4-aryl-5,6,7,8-tetrahydrobenzo-4*H*-pyran-3-carbonitrile was heated in the presence of a catalytic amount of DABCO instead of reported catalysts under reported conditions. Results of reaction with alternative catalyst were satisfied to the reported methods. The corresponding 4*H*-pyrans derivatives **3** were obtained in good to excellent yields. The results are summarized in Table 1.

With the above results in hand, a variety of bisarylidene-cyclohexanone at first synthesized [33] from aromatic aldehydes, possessing both electron-donating and electron-withdrawing groups. Then these compounds were employed in synthesis of 4*H*-pyrans formation and in all the cases, the yields were very good (Scheme 1, Table 1).

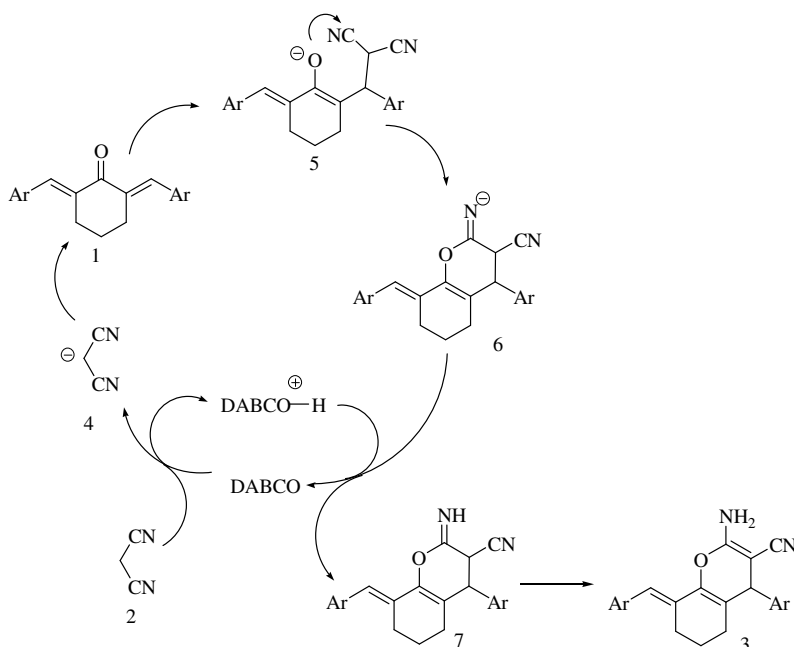
Pervious methods for synthesis of 2-amino-8-arylidene-4-aryl-5,6,7,8-tetrahydrobenzo-4*H*-pyran-3-carbonitrile suffer from drawbacks such as using of microwave irradiation, long reaction time, high temperatures and expensive catalyst. All the known products were characterized by comparing their physical and spectral (IR, ¹H NMR and ¹³C NMR) data with those of the samples reported in the literature. The data for unknown compounds (Table 1, **3e-3n**) are reported in this paper. As shown in Table 1, bisarylidene-cyclohexanones with electron-withdrawing groups on the aromatic ring led to products with slightly higher yields than bisarylidene-cyclohexanones with electron-donating groups.



Scheme 2. Major and minor product as one pair diastereoisomers.

Just as seen in the Scheme 2, in the synthesis of new compounds (**3h-3n**), two stereocenters are formed thus we expect that the product is mixture of two diastereomers. This subject is observed in the ^1H and ^{13}C NMR spectra obviously so ^1H and ^{13}C NMR spectra of these compounds are specified for two isomers separately.

The possible mechanism for the formation of compound **3** have been as following, initially using of an acid/base catalytic reaction between DABCO and malononitrile, a carboanion intermediate **4** has been produced. Then compound **5** was afforded *via* a Michael adduct of intermediate **4** to bisarylidencyclohexanone **1**. After that compound **6** as a result of nucleophilic attack of the OH group on the cyano (CN) moiety take place according to Scheme 3 *via* cyclization. Finally through tautomerisation from intermediate **6** products **3** was obtained.



Scheme 3. A plausible mechanism for the formation of compounds **3**.

The method offers several advantages, such as omitting any toxic solvent or catalyst, very simple work-up procedure without using any chromatographic method, and improving the yields. Starting materials are inexpensive and commercially available.

ACKNOWLEDGEMENTS

Authors gratefully acknowledge the Teacher Training University and Islamic Azad University-Marvdasht Branch for supporting of this work.

REFERENCES

- Morinaka, Y.; Takahashi, K. *Jpn. Patent* JP52017498, **1977**.
- Hafez, E.A.A.; Elnagdi, M.H.; Elagamey, A.G.A.; El-Taweel, F.M.A.A. *Heterocycles* **1987**, 26, 903.
- Li, A.H.; Ji, X.D.; Kim, H.S.; Melman, N.; Jacobson, K.A. *Drug Devel. Res.* **1999**, 48, 171.
- Urbahns, K.; Horvth, E.; Stasch, J.P.; Mauler, F. *Bioorg. Med. Chem. Lett.* **2003**, 13, 2637.
- Fravel, B.W. *Pyrans and Their Benzo Derivatives: Applications in Comprehensive Heterocyclic Chemistry III*, Katritzky, A.R.; Ramsden, C.A.; Scriven, E.F.V.; Taylor, R.J.K. (Eds.); Pergamon Press: Oxford; **1995**.
- Dong, Y.; Shi, Q.; Nakagawa-Goto, K.; Wu, P.-C.; Morris-Natschke, S.L.; Brossi, A.; Bastow, K.F.; Lang, J.-Y.; Hung, M.-C.; Lee, K.-H. *Bioorg. Med. Chem.* **2010**, 18, 803.
- El-Saghier, A.M.M.; Naili, M.B.; Rammash, B.Kh.; Saleh, N.A.; Kredan, K.M. *Arkivoc* **2007**, 83.
- Kumar, R.R.; Perumal, S.; Senthilkumar, P.; Yogeewari, P.; Sriram, D. *Bioorg. Med. Chem. Lett.* **2007**, 17, 6459.
- Geen, G.R.; Evans, J.M.; Vong, A.K. *Pyrans and Their Benzo Derivatives: Applications in Comprehensive Heterocyclic Chemistry II*, Katritzky, A.R.; Rees, C.W.; Scriven, E.F.V. (Eds.); Pergamon Press: Oxford; **1995**.
- O'Callaghan, C.N.; McMurry, T.B.H.; O'Brien, J.E. *J. Chem. Soc., Perkin Trans. I* **1995**, 417.
- Ibrahim, N.S. *Heterocycles* **1986**, 24, 935.
- Martin, N.; Seoane, C.; Soto, J.L. *Tetrahedron* **1988**, 44, 5861.
- Heber, D.; Stoyanov, E.V. *Synthesis* **2003**, 227.
- Balalaie, S.; Sheikh-Ahmadi, M.; Bararjanian, M. *Catal. Commun.* **2007**, 8, 1724.
- Banerjee, S.; Horn, A.; Khatri, H.; Sereida, G. *Tetrahedron Lett.* **2011**, 52, 1878.
- Abdel-latif, F.F.; Mashaly, M.M.; Gawish, E.H. *J. Chem. Res.* **1995**, 5, 1220.
- Singh, K.; Singh, J.; Singh, H. *Tetrahedron* **1996**, 52, 14273.
- Tu, S.T.; Gao, Y.; Guo, C.; Shi, D.; Lu, Z. *Synth. Commun.* **2002**, 32, 2137.
- Wang, X.S.; Shi, D.Q.; Tu, S.T.; Yao, C.S. *Synth. Commun.* **2003**, 33, 119.
- Li, J.T.; Xu, W.Z.; Yang, L.C.; Li, T.S. *Synth. Commun.* **2004**, 34, 4565.
- Jiu, T.S.; Wang, A.Q.; Wang, X.; Zhang, J.S.; Li, T.S. *Synlett* **2004**, 871.
- Jiang, Z.Q.; Ji, S.J.; Lu, J.; Yang, J.M. *Chin. J. Chem.* **2005**, 23, 1085.
- Balalaie, S.; Bararjanian, M.; Amani, A.M.; Movassagh, B. *Synlett* **2006**, 263.
- Ranu, B.C.; Banerjee, S. *Indian J. Chem. Soc.* **2008**, 47, 1108.
- Babu, N.S.; Pasha, N.; Rao, V.K.T.; Prasad, S.P.S.; Lingaiah, N. *Tetrahedron Lett.* **2008**, 49, 2730.
- Yu, L.-Q.; Liu, F.; You, Q.-D. *Org. Prep. Proced. Int.* **2009**, 41, 77.
- Pore, D.M.; Undale, K.A.; Dongare, B.B.; Desai, U.V. *Catal. Lett.* **2009**, 132, 104.
- Gurumurthi, S.; Sundari, V.; Valliappan, R. *Eur. J. Chem.* **2009**, 6, 466.
- Jin, T.-S.; Liu, L.-B.; Zhao, Y.; Li, T.-S. *Synth. Commun.* **2005**, 35, 1859.
- Zhou, J.-F. *Synth. Commun.* **2003**, 33, 99.
- Wang, X.-S.; Shi, D.-Q.; Tu, S. *J. Chin. J. Chem.* **2004**, 122.
- (a) Rostamizadeh, Sh.; Amani, M.A.; Mahdavinia, G.H.; Amiri, G.; Sepehrian, H. *Ultrasound Sonochem.* **2010**, 17, 306; (b) Rostamizadeh, Sh.; Amani, M.A.; Mahdavinia, G.H.; Sepehrian, H.; Ebrahimi, S. *Synthesis* **2010**, 1356.
- Bigdeli, M.A.; Mahdavinia, G.H.; Jafari, S.; Hazarkhani, H. *Catal. Commun.* **2007**, 8, 2228.