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Palladium-catalyzed three-component cyclization of 2-bromocyclohex-1-enecarboxylic acids with carbon monoxide and arylhydrazines leading to 2-anilinohydroisoindoline-1,3-diones

Il Chul Yoon and Chan Sik Cho*

2-Bromocyclohex-1-enecarboxylic acids are carbonylatively cyclized with arylhydrazines or their hydrochlorides in tetrahydrofuran at 120 °C under carbon monoxide pressure in the presence of a catalytic amount of $PdCl_2$ and 1,3-bis(diphenylphosphino) propane along with Et_3N to give 2-anilinohydroisoindoline-1,3-diones. Copyright © 2015 John Wiley & Sons, Ltd.

Keywords: 2-bromocyclohex-1-enecarboxylic acids; carbonylation and cyclization; arylhydrazines; 2-anilinohydroisoindoline-1,3-diones; palladium catalyst

Introduction

It is known that 2-anilinoisoindoline-1,3-diones and their hydro analogues exhibit biological activities such as anticancer[1] and herbicidal activities (Scheme 1).[2] 2-(Phenylamino)isoindoline-1,3-dione is also used as a precursor for the preparation of anti-inflammatory products.[3] Such scaffolds are generally synthesized by the reaction of the corresponding phthalic and maleic anhydrides with arylhydrazines.[4,5] As part of our continuing studies directed towards transition metal-catalyzed cyclization reactions of β-bromo-α,β-unsaturated aldehydes and their derivatives, we have identified several new methods for the synthesis of various carbonyl group-containing heterocycles via palladium-catalyzed carbonylative cyclization (carbonylation followed by cyclization) under carbon monoxide pressure.[6–19] β-Bromo-α,β-unsaturated aldehydes and their derivatives are readily prepared from α-methylene group-containing ketones by bromination under Vilsmeier–Haack conditions[20,21] and subsequent transformation, and the products can serve as valuable building blocks for the construction of various cyclic compounds.[22–38] Among such carbonlative cyclization reactions, we recently have shown that β-bromo-α,β-unsaturated carboxylic acids can be carbonylatively cyclized with 2,2-dimethylhydrazine under carbon monoxide pressure in the presence of a palladium catalyst to give 1-(dimethylamino)-1*H*-pyrrole-2,5-diones.[39] The present work arose during the course of the application of this protocol to the reaction with arylhydrazines. This report describes a facile method for the synthesis of 2-anilinohydroisoindoline-1,3-diones by palladium-catalyzed carbonylative cyclization of 2-bromocyclohex-1-enecarboxylic acids with arylhydrazines or arylhydrazine hydrochlorides under carbon monoxide pressure.

Results and Discussion

Table 1 gives several results for the attempted carbonylative cyclization of 2-bromocyclohex-1-enecarboxylic acid (**1a**) with phenylhydrazine (**2a**), leading to 2-(phenylamino)-4,5,6,7-tetrahydro-2*H*-isoindole-1,3-dione (**3a**) under various conditions such as molar ratio of **2a** to **1a**, ligand, solvent, reaction temperature and time, and CO pressure. Treatment of **1a** with an equimolar amount of **2a** under CO (10 atm) in THF at 120 °C for 3 h in the presence of a catalytic amount of $PdCl_2$ and 1,3-bis (diphenylphosphino)propane (dppp) along with Et_3N affords **3a** in 23% isolated yield with several unidentifiable products (entry 1). The carbonylative *endo*-cyclized product **4** is not produced at all regardless of an effort to isolate such a scaffold from the reaction mixture. The yield of **3a** is considerably affected by the molar ratio of **2a** to **1a**. A ratio of [**2a**]/[**1a**] = 3 is desirable from an atom economy point of view, not shown in Table 1, since a higher molar ratio ([**2a**]/[**1a**] = 4–5) results in rather lower yield of **3a** (47–51% yields; entries 1–3). Prolonging the reaction time gives no improvement in the yield of **3a** (entry 4). No significant change of the yield of **3a** is observed with dilution of the reaction mixture (entry 5). Either lower reaction temperature or CO pressure results in a decreased yield of **3a** (entries 6 and 7). The reaction also proceeds in the presence of various other phosphorus ligands, such as PPh_3, 1,2-bis(diphenylphosphino)ethane (dppe), 1,4-bis(diphenylphosphino)butane (dppb) or 1,1′-bis (diphenylphosphino)ferrocene (dppf), under the employed conditions, but the yields of **3a** are generally lower than that obtained in the presence of dppp (entries 8–11). As a result, after further tuning with several solvents and catalyst amount (entries 12–15), the best result in terms of both product yield and complete conversion of **1a** is obtained using the standard set of reaction conditions shown in entry 3 of Table 1.

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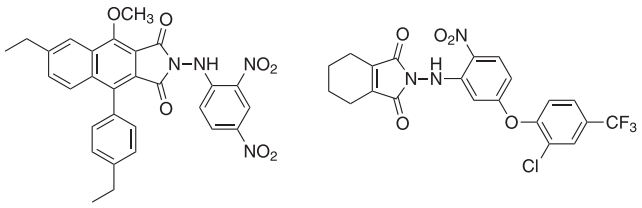
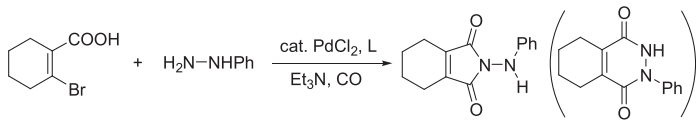


Scheme 1. Biologically active compounds.

With the optimum reaction conditions in hand, various 2-bromocyclohex-1-enecarboxylic acids **1** were subjected to reaction with arylhydrazines (or arylhydrazine hydrochlorides) **2** to investigate the scope of the reaction. Several representative results are summarized in Table 2.[40] In view of the availability of the arylhydrazine counterpart, it is desirable to use arylhydrazine hydrochloride since most commercially available arylhydrazines are sold as their hydrochloride salts. Similar treatment of **1a** with phenylhydrazine hydrochloride (condition B, **2a**) for 20 h under the employed conditions affords **3a** in 46% isolated yield. Lower reaction rate and yield are observed with arylhydrazine hydrochlorides **2**. 2-Bromocyclohex-1-enecarboxylic acid (**1a**) is readily carbonylatively cyclized with an array of arylhydrazine hydrochlorides (**2b–f**) to give the corresponding 2-anilinohydroisoindoline-1,3-diones **(3b–f)** in the range 37–55% isolated yields and the product yield varies with the position and electronic nature of the substituent on **2**. Judging from the reaction of **1a** with **2b–d** having electron-donating methyl substituent, the product yield has relevance to the position of the substituent on the aromatic ring of **2b–d**. With *meta*-methyl-substituted **2c**, the product yield is generally lower than that when *ortho*-methyl-substituted **2b** and *para*-methyl-substituted **2d** are used. With **2e** having an electron-donating methoxy substituent, the product yield is lower than when **2f** having an electron-withdrawing Cl substituent is used under condition B. 2-Bromocyclohex-1-enecarboxylic acids having methyl and phenyl substituents on the cyclohexane ring, **1b** and **1c**, were also carbonylatively cyclized with **2a** under the employed condition A to give 5-methyl- and 5-phenyl-2-(phenylamino)-4,5,6,7-tetrahydro-1*H*-isoindole-1,3(2*H*)-diones (**3 g** and **3 h**) in 46 and 31% yields, respectively. From the reaction of **1b** with **2a**, **3 g** is formed in similar yields under both conditions A and B. To test for the effect of the position of bromide and carboxy groups on 2-bromocyclohex-1-enecarboxylic acids, **1d** and **1e** were employed. The carbonylative cyclization readily takes place with both **1d** and **1e** irrespective of their position. However, 2-(4-tolylamino)-1*H*-benzo[*e*]isoindole-1,3(2*H*)-dione (**3i**) is produced by dehydrogenation of the initially formed 2-(4-tolylamino)-4,5-dihydro-1*H*-benzo[*e*]isoindole-1,3(2*H*)-dione under the employed conditions. The mass spectrum of **3i** shows peaks at $m/z = 302$ (M^+, 100% intensity) and 303 ($M^+ + 1$, 23% intensity). Similar dehydrogenation was observed in our recent work on the coupling and cyclization of β-bromo-α,β-unsaturated amides with formamide.[37]

Product **3b** was chosen for structural identification and confirmed from its IR, mass, ^{1}H NMR and ^{13}C NMR spectra. The IR spectrum exhibits a characteristic absorption at 1724 cm^{-1} attributed to the carbonyl group of **3b**. The high-resolution mass spectrum displays a peak at $m/z = 256.1209$ (M^+). The ^{1}H NMR and

Table 1. Optimization of conditions for the reaction of **1a** with **2a**[a]

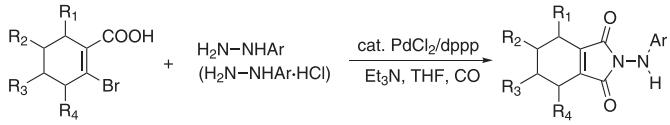


1a **2a** **3a** **4**

Entry	[**2a**]/[**1a**]	Ligand	Solvent	Yield (%)
1	1	dppp	THF	23
2	2	dppp	THF	53
3	3	dppp	THF	57
4[b]	3	dppp	THF	52
5[c]	3	dppp	THF	50
6[d]	3	dppp	THF	45
7[e]	3	dppp	THF	49
8	3	PPh_3	THF	45
9	3	dppe	THF	15
10	3	dppb	THF	41
11	3	dppf	THF	47
12	3	dppp	Dioxane	31
13	3	dppp	MeCN	13
14	3	dppp	DMF	2
15[f]	3	dppp	THF	25

[a]Reaction conditions: **1a** (0.5 mmol), $PdCl_2$ (0.025 mmol), ligand (bidentate ligands: 0.03 mmol; PPh_3: 0.05 mmol), Et_3N (2 mmol), solvent (10 ml), CO (10 atm), 120 °C, 3 h, unless otherwise stated.
[b]For 8 h.
[c]THF (20 ml).
[d]At 60 °C.
[e]Under CO (5 atm).
[f]$PdCl_2$ (0.01 mmol).

Table 2. Palladium-catalyzed synthesis of 2-(arylamino)-4,5,6,7-tetrahydro-2*H*-isoindole-1,3-diones **3** from β-bromo-α, β-unsaturated ketones **1** and arylhydrazines (or arylhydrazine hydrochlorides) **2**[a]



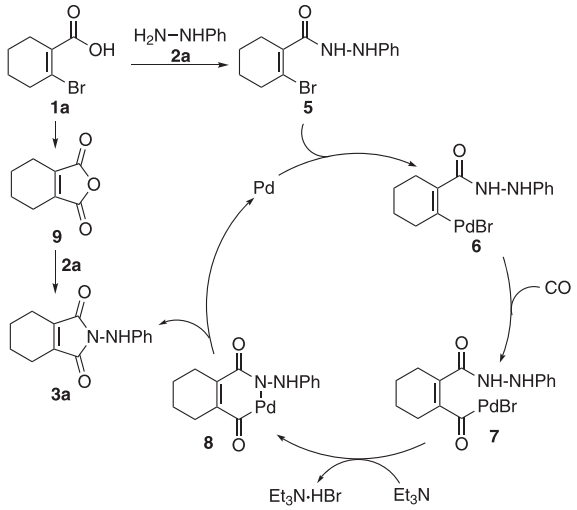
2a Ar = Ph
2b Ar = 2-MeC_6H_4
2c Ar = 3-MeC_6H_4
2d Ar = 4-MeC_6H_4
2e Ar = 4-$MeOC_6H_4$
2f Ar = 4-ClC_6H_4

1					**2**	Condition[b]	Product	Yield (%)
R^1	R^2	R^3	R^4					
H	H	H	H	**1a**	**2a**	A	**3a**	57
H	H	H	H	**1a**	**2a**	B	**3a**	46
H	H	H	H	**1a**	**2b**	B	**3b**	46
H	H	H	H	**1a**	**2c**	B	**3c**	37
H	H	H	H	**1a**	**2d**	B	**3d**	48
H	H	H	H	**1a**	**2e**	B	**3e**	41
H	H	H	H	**1a**	**2f**	B	**3f**	55
H	Me	H	H	**1b**	**2a**	A	**3 g**	46
H	Me	H	H	**1b**	**2a**	B	**3 g**	44
H	Ph	H	H	**1c**	**2a**	A	**3 h**	31
H	H	Benzofused		**1d**	**2d**	B	**3i**[c]	40
Benzofused		H	H	**1e**	**2d**	B	**3i**[c]	43

[a]Reaction conditions: **1** (0.5 mmol), **2** (1.5 mmol), $PdCl_2$ (0.025 mmol), dppp (0.03 mmol), THF (10 ml), CO (10 atm), 120 °C.
[b]Condition A: arylhydrazine, Et_3N (2 mmol), for 3 h; condition B: arylhydrazine hydrochloride, Et_3N (3.5 mmol), for 20 h.
[c]2-(4-Methylphenylamino)-2*H*-benzo[*e*]isoindole-1,3-dione.

^{13}C NMR spectra of **3b** show characteristic signals with appropriate chemical shifts detailed with the spectroscopic data in the Experimental section.

As to the reaction pathway, although it is not yet fully understood, this seems to proceed via an initial formation of hydrazide **5** by the condensation between **1a** and **2a** (Scheme 2). Oxidative addition of a carbon–bromide bond of **5** to palladium (0) produces a vinyl intermediate **6**, where carbon monoxide coordination to palladium and then vinyl migration from palladium to the carbon of carbon monoxide occur to give an acylpalladium(II) intermediate (**7**). This is followed by cyclization due to extrusion of HBr by Et_3N to produce palladacycle **8**, which can reductively eliminate to afford **3a**. Alternatively, it appears that **3a** is also produced by the displacement of initially formed maleic anhydride **9** by phenylhydrazine **2a**.[19] We confirmed in a separate experiment that maleic anhydride **9** reacted with **2a** in THF at 120 °C for 3 h to give the product **3a** in 70% yield.[4,5,41]



Scheme 2. Proposed catalytic cycle.

Conclusions

In summary, we have demonstrated that 2-bromocyclohex-1-enecarboxylic acids, which are readily prepared from cyclohexanones in two steps, can be carbonylatively cyclized with arylhydrazines or their hydrochlorides to give 2-anilinohydroisoindoline-1, 3-diones in the presence of $PdCl_2$ and dppp along with Et_3N. The present reaction provides a promising route for the synthesis of valuable heterocycles from readily available ketones. Further study of synthetic applications to heterocycles starting from ketones is currently under way.

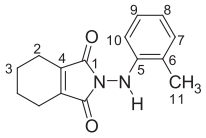
Experimental

^1H NMR and ^{13}C NMR (400 and 100 MHz) spectra were recorded with a Bruker Avance Digital 400 spectrometer using tetramethylsilane as an internal standard. Melting points were determined with a Stanford Research Inc. MPA100 automated melting point apparatus. High-resolution mass spectrometry (HRMS) was performed with a Jeol JMS-700 spectrometer at the Korea Basic

Science Center, Daegu, Korea. The isolation of pure products was carried out via thin-layer (silica gel 60 GF_{254}, Merck) chromatography. The starting 2-bromocyclohex-1-enecarboxylic acids were prepared via two steps from the corresponding cyclohexanones according to literature procedures.[20,21,40] Commercially available organic and inorganic compounds were used without further purification.

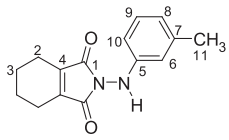
Typical Procedure for Palladium-Catalyzed Carbonylative Cyclization of 2-Bromocyclohex-1-enecarboxylic Acids with Arylhydrazines (or their Hydrochlorides)

To a 50 ml stainless steel autoclave were added 2-bromocyclohex-1-enecarboxylic acid (**1a**; 0.103 g, 0.5 mmol), phenylhydrazine (**2a**; 0.162 g, 1.5 mmol), $PdCl_2$ (0.004 g, 0.025 mmol), dppp (0.012 g, 0.03 mmol), Et_3N (0.202 g, 2.0 mmol) and THF (10 ml). After the system was flushed and then pressurized with CO to 10 atm, the reaction mixture was heated to react at 120 °C for 3 h. The reaction mixture was filtered through a short silica gel column (ethyl acetate) to eliminate inorganic salts. Removal of the solvent left a crude mixture, which was separated by thin-layer chromatography (silica gel, ethyl acetate–hexane = 1:2) to give 2-(phenylamino)-4,5,6,7-tetrahydro-2*H*-isoindole-1,3-dione (**3a**; 0.069 g, 57%). Except for known **3a**,[39] all new products prepared using the procedure outlined above were characterized spectroscopically as shown below.



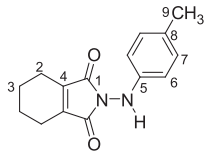
*2-(2-Methyphenylamino)-4,5,6,7-tetrahydro-2H-isoindole-1,3-dione (**3b**)*

Semisolid. IR (ATR): 1724 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.79–1.82 (m, 4H, $-(CH_2)_2-$), 2.30 (s, 3H, CH_3), 2.37–2.40 (m, 4H, allylic $2CH_2$), 5.85 (s, 1H, N*H*), 6.52 (d, J_{HH} = 7.8 Hz, 1H, H10), 6.83–6.87 (m, 1H, H8), 7.05–7.09 (m, 2H, H7 and H9). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 17.10 (C11), 20.20 (C3), 21.27 (C2), 112.12 (C10), 121.69 (C6), 123.16 (C8), 127.09 (C9), 130.83 (C7), 140.56 (C4), 144.06 (C5), 169.21 (C1), assignments to C6–C8 are interchangeable. HRMS (EI). Anal. Calcd for $C_{15}H_{16}N_2O_2$ (M^+): 256.1212. Found: 256.1209. Anal. Calcd for $C_{15}H_{16}N_2O_2$ (%): C, 70.29; H, 6.29; N, 10.93. Found (%): C, 70.10; H, 6.18; N, 10.98.



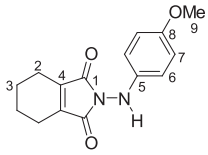
*2-(3-Methyphenylamino)-4,5,6,7-tetrahydro-2H-isoindole-1,3-dione (**3c**)*

Semisolid. IR (ATR): 1724 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.72–1.75 (m, 4H, $-(CH_2)_2-$), 2.20 (s, 3H, CH_3), 2.30–2.36 (m, 4H, allylic $2CH_2$), 5.26 (br s, 1H), 6.46–6.49 (m, 2H, H6 and H8), 6.66–6.68 (m, 1H, H10), 7.00–7.04 (m, 1H, H9). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 20.25 (C11), 21.32 (C3), 21.69 (C2), 111.05 (C10), 114.55 (C6), 123.03 (C8), 129.24 (C9), 139.36 (C7), 140.59 (C4), 146.24 (C5), 169.28 (C1), assignments to C2, C3 and C11 are interchangeable, assignments to C6 and C10 are interchangeable. HRMS (EI). Anal. Calcd for $C_{15}H_{16}N_2O_2$ (M^+): 256.1212. Found: 256.1210. Anal. Calcd for $C_{15}H_{16}N_2O_2$ (%): C, 70.29; H, 6.29; N, 10.93. Found (%): C, 70.17; H, 6.25; N, 10.94.



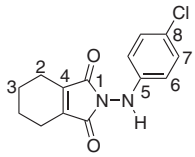
*2-(4-Methyphenylamino)-4,5,6,7-tetrahydro-2H-isoindole-1,3-dione (**3d**)*

Semisolid. IR (ATR): 1721 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.78–1.81 (m, 4H, $-(CH_2)_2-$), 2.25 (s, 3H, CH_3), 2.36–2.39 (m, 4H, allylic $2CH_2$), 5.89 (s, 1H, N*H*), 6.66–6.69 (m, 2H, H6), 7.02 (d, J_{HH} = 8.0 Hz, 2H, H7). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 20.23 (C9), 20.76 (C2), 21.33 (C3), 114.32 (C6), 129.89 (C7), 131.62 (C8), 140.57 (C5), 143.92 (C4), 169.31 (C1), assignments to C2, C3 and C9 are interchangeable, assignments to C4 and C5 are interchangeable. HRMS (EI). Anal. Calcd for $C_{15}H_{16}N_2O_2$ (M^+): 256.1212. Found: 256.1209. Anal. Calcd for $C_{15}H_{16}N_2O_2$ (%): C, 70.29; H, 6.29; N, 10.93. Found (%): C, 70.13; H, 6.22; N, 10.91.



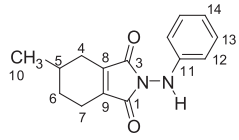
*2-(4-Methoxyphenylamino)-4,5,6,7-tetrahydro-2H-isoindole-1,3-dione (**3e**)*

Solid; m.p. 93–94 °C. IR (ATR): 1709 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.79–1.82 (m, 4H, $-(CH_2)_2-$), 2.39–2.42 (m, 4H, allylic $2CH_2$), 3.81 (s, 3H, CH_3), 6.94–6.98 (m, 2H, H6), 7.20–7.24 (m, 2H, H7), NH signal was not observed. ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 20.28 (C2), 21.48 (C3), 55.58 (C9), 114.46 (C6), 124.62 (C5), 127.68 (C7), 141.76 (C4), 158.88 (C8), 170.39 (C1). Anal. Calcd for $C_{15}H_{16}N_2O_3$ (%): C, 66.16; H, 5.92; N, 10.29. Found (%): C, 65.97; H, 5.88; N, 10.27.



*2-(4-Chlorophenylamino)-4,5,6,7-tetrahydro-2H-isoindole-1,3-dione (**3f**)*

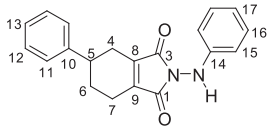
Solid; m.p. 138–140 °C. IR (ATR): 1736 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.80–1.83 (m, 4H, $-(CH_2)_2-$), 2.38–2.41 (m, 4H, allylic $2CH_2$), 5.94 (s, 1H, N*H*), 6.67–6.71 (m, 2H, H6), 7.16–7.24 (m, 2H, H7). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 20.31 (C3), 21.30 (C2), 115.22 (C6), 127.06 (C8), 129.43 (C7), 140.82 (C5), 144.89 (C4), 169.07 (C1), assignments to C4 and C5 are interchangeable. Anal. Calcd for $C_{14}H_{13}ClN_2O_2$ (%): C, 60.77; H, 4.74; N, 10.12. Found (%): C, 60.58; H, 4.66; N, 10.15.



*5-Methyl-2-(phenylamino)-4,5,6,7-tetrahydro-2H-isoindole-1,3-dione (**3 g**)*

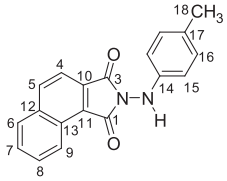
Semisolid. IR (ATR): 1721 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.67–1.72 (m, 4H, CH_3 and C*H*), 1.80–1.85 (m, 2H, CH_2),

2.56–2.59 (m, 4H, allylic 2CH_2), 6.03 (s, 1H, N*H*), 6.72–6.75 (m, 2H, H12), 6.90–6.94 (m, 1H, H14) 7.18–7.23 (m, 2H, H13). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 25.04 (C10), 26.63 (C6 and C7), 30.26 (C4 and C5), 113.87 (C12), 122.07 (C14), 129.36 (C13), 141.58 (C8 and C9), 146.13 (C11), 170.14 (C1 and C3). HRMS (EI). Anal. Calcd for $C_{15}H_{16}N_2O_2$ (M^+): 256.1212. Found: 256.1210. Anal. Calcd for $C_{15}H_{16}N_2O_2$ (%): C, 70.29; H, 6.29; N, 10.93. Found (%): C, 70.00; H, 6.18; N, 10.97.



*5-Phenyl-2-(phenylamino)-4,5,6,7-tetrahydro-2H-isoindole-1,3-dione (**3 h**)*

Semisolid. IR (ATR): 1728 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.82–1.92 (m, 1H, CH_2/2), 2.16–2.21 (m, 1H, CH_2/2), 2.40–2.52 (m, 2H, allylic CH_2), 2.60–2.67 (m, 1H, allylic CH_2/2), 2.75–2.81 (m, 1H, allylic CH_2/2), 2.90–2.97 (m, 1H, C*H*), 6.04 (s, 1H, N*H*), 6.75–6.78 (m, 2H, H15), 6.91–6.95 (m, 1H, H17), 7.20–7.28 (m, 5H, H11, H13, H16), 7.33–7.37 (m, 2H, H12), assignments to H11, H12 and H16 are interchangeable. ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 21.03 (C7), 27.87 (C6), 28.96 (C5), 39.33 (C4), 113.91 (C15), 122.15 (C17), 126.90 (C13), 127.04 (C11), 128.94 (C12), 129.44 (C16), 140.36 (C8 and C9), 144.37 (C10), 146.20 (C14), 168.89 (C1), 168.92 (C3), assignments to C1 and C3 are interchangeable, assignments to C11–C13 are interchangeable. HRMS (EI). Anal. Calcd for $C_{20}H_{18}N_2O_2$ (M^+): 318.1368. Found: 318.1369. Anal. Calcd for $C_{20}H_{18}N_2O_2$ (%): C, 75.45; H, 5.70; N, 8.80. Found (%): C, 75.27; H, 5.58; N, 8.84.



*2-(4-Methyphenylamino)-2H-benzo[e]isoindole-1,3-dione (**3i**)*

Solid; m.p. 166–168 °C. IR (ATR): 1724 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.25 (s, 3H, CH_3), 6.18 (s, 1H, N*H*), 6.79–6.83 (m, 2H, H15), 7.04 (d, J_{HH} = 8.1 Hz, 2H, H16), 7.67–7.76 (m, 2H, H7 and H8), 7.91 (d, J_{HH} = 8.3 Hz, 1H, H6), 7.97 (d, J_{HH} = 8.1 Hz, 1H, H5), 8.23 (d, J_{HH} = 8.1 Hz, 1H, H4), 8.91–8.94 (m, 1H, H9). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 20.81 (C18), 114.63 (C15), 118.92 (C9), 125.27 (C4), 125.49 (C16), 128.22 (C7), 129.01 (C12), 129.33 (C6), 129.38 (C17), 130.05 (C5 and C8), 132.00 (C13), 135.82 (C11), 137.02 (C10), 143.83 (C14), 167.38 (C1), 168.08 (C3), assignments to C1 and C3 are interchangeable, assignments to C10 and C11 are interchangeable, assignments to C4–C8, C12, C16 and C17 are interchangeable. HRMS (EI). Anal. Calcd for $C_{19}H_{14}N_2O_2$ (M^+): 302.1055. Found: 302.1053. Anal. Calcd for $C_{19}H_{14}N_2O_2$ (%): C, 75.48; H, 4.67; N, 9.27. Found (%): C, 75.30; H, 4.59; N, 9.31.

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