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Synthesis of 1′-aryl-2′-(2-oxoindolin-3-yl)spiro[indoline-3,5′-pyrroline]-2,3′-dione via one-pot reaction of arylamines, acetone, and isatins

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ABSTRACT

An efficient synthetic method for 1′-aryl-2′-(2-oxoindolin-3-yl)spiro[indoline-3,5′-pyrroline]-2,3′-diones was successfully developed via the one-pot domino reaction of arylamines, acetone, and isatins in acetic acid. The reaction mechanism involved the sequential Michael addition and ring closure of the in situ formed 3-*N*-aryliminoisatin and isatylidene acetone.

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The spirooxindole system is the core structure of many pharmacological agents and natural alkaloids.[1,2] As a consequence, a number of methods have been reported for the preparation of spirooxindole-fused heterocycles.[3,4] Recent synthetic methods to access spirocyclic oxindoles include cycloaddition,[5–7] Morita–Baylis–Hillman reaction,[8,9] and other cyclization reactions.[10] Isatin derivatives are important precursors of spirocyclic oxindoles and many naturally occurring oxindole alkaloids.[11,12] In the past few years the multicomponent reactions or domino reactions based on the versatile reactivity of isatins have become the most widely used methods for the synthesis of various spirooxindoles.[13–16] As our program on new multicomponent reactions for the synthesis of heterocyclic compounds,[17,18] herein we wish to report the efficient synthesis of the novel functionalized 1′-aryl-2′-(2-oxoindolin-3-yl)spiro[indoline-3,5′-pyrroline]-2,3′-diones via the one-pot domino reaction of arylamines, acetone, and isatins in acetic acid.

It has been known that the domino reactions of isatins with Huisgen's zwitterions formed in situ from isoquinoline and acetylenic esters have become the efficient synthetic procedures for constructing versatile spirooxindole systems.[19,20] Perumal and coworkers successfully reported the synthesis of spiro[indole-3,4′-pyridines] derivatives by the four-component reaction of arylamine, acetylenedicarboxylate, malononitrile, and isatin.[21] The publication of these works prompted us to envisage using other functionalized isatins such as isatylidene acetone or isatylidene chalcone to react with Huisgen's zwitterions for spirooxindoles. In our initial endeavor, we have investigated a one-pot three-component reaction of isatin, acetone, and β-arylaminobutenedicarboxylate, which was prepared in situ from the addition of arylamine to acetylenedicarboxylate in acetic acid. After workup, a yellow solid was obtained in about 40% yield. Its structure was assigned as 1′-aryl-2′-(2-oxoindolin-3-yl)spiro[indoline-3,5′-pyrroline]-2,3′-dione. There is no unit of dimethyl acetylenedicarboxylate in its molecule, which clearly indicated that only arylamine, acetone, and isatin reacted as three-components to form the obtained product. This interesting result encouraged us to examine the three-component reaction of arylamine, acetone, and isatin of catalyst, solvent, temperature, and adding sequences of substrates. The best result was obtained by carrying out the three-component reaction in domino type and using acetic acid. Thus *p*-methoxyaniline first reacted with isatin in acetic acid at room temperature for 2 h for the formation of the active intermediate 3-*N*-aryliminoisatin. Then second molar isatin and excess acetone were added and the reaction proceeded smoothly at room temperature for about 3 h to give the desired 1′-*p*-methoxyphenyl-2′-(2-oxoindolin-3-yl)spiro[indoline-3,5′-pyrroline]-2,3′-dione (**1a**) in 70% yield (Table 1, entry 1).[22] Then 5-methyl, 5-chloro-, 5-fluoroisatins and various arylamines with different substituents were utilized in this one-pot domino reaction under the similar reaction conditions. The results are shown in Table 1. From these results we could see that all the reactions proceeded smoothly to afford the corresponding spiro compounds (**1b**–**1k**) in good yields. Arylamines with electron-donating methyl and methoxyl groups gave better yields than those of *p*-chloroaniline. The structures of spiro compounds were fully characterized by ^{1}H and ^{13}C NMR, HPLC/MS, HRMS, and IR

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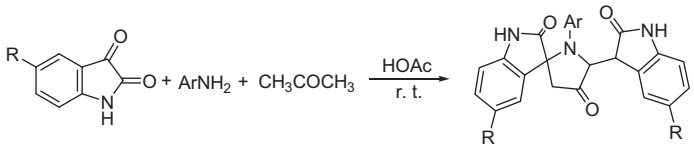
Table 1
One-pot synthesis of 1′-aryl-2′-(2-oxoindolin-3-yl)spiro[indoline-3,5′-pyrroline]-2,3′-diones



Entry	Compound	Ar	R	Yield (%)
1	**1a**	*p*-$CH_3OC_6H_4$	H	70
2	**1b**	*p*-$CH_3OC_6H_4$	CH_3	78
3	**1c**	*p*-$CH_3OC_6H_4$	Cl	71
4	**1d**	*p*-$CH_3OC_6H_4$	F	70
5	**1e**	*p*-$CH_3C_6H_4$	H	62
6	**1f**	*p*-$CH_3C_6H_4$	CH_3	65
7	**1g**	*p*-$CH_3C_6H_4$	F	64
8	**1h**	*m*-$CH_3C_6H_4$	CH_3	60
9	**1i**	C_6H_5	CH_3	70
10	**1j**	*p*-ClC_6H_4	H	52
11	**1k**	*p*-ClC_6H_4	CH_3	56

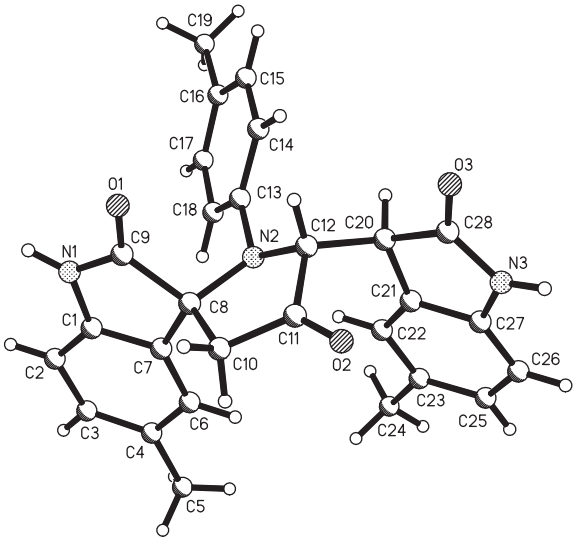
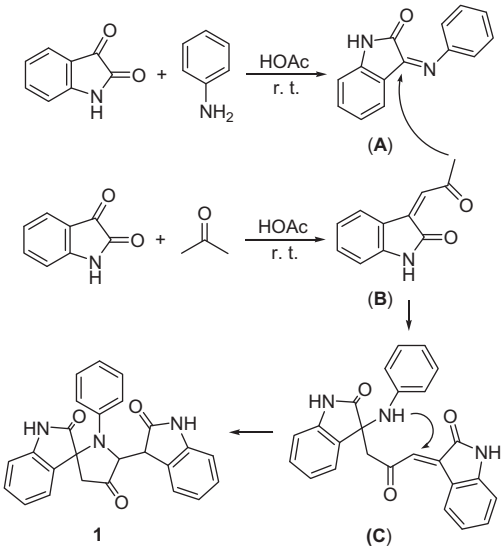


Figure 1. Molecular structure of spiro compound **1f**.



Scheme 1. The proposed reaction mechanism.

spectra, further confirmed by single-crystal X-ray diffraction determination of compound **1e** (Fig. 1). ^{1}H NMR spectra of the **1a**–**1k** clearly indicated that only one diastereomer exists in the formed product. As for example, in ^{1}H NMR spectra of **1a**, the two NH units in two pyrrole rings show two singlets at 10.50 and 10.31 ppm. The proton at 2′-position shows a doublet at 5.08 ppm and two protons at 4′-position display two doublets at 2.79 and 2.68 ppm with germinal coupling constants J = 18.0 Hz. The proton at 3-position in 2-oxoindolin-3-yl group also shows a doublet at 3.45 ppm.

To evaluate the scope of this three-component reaction further, other reactive ketones such as butanone, 1-phenylacetone, and 1,3-diphenylacetone were also tested. But the results of these reactions were very disappointing. Only 3-*N*-aryliminoisatin could be separated from the reaction mixture. At present an exact mechanism for the formation of spiro[indoline-3,5′-pyrroline]-2,3′-diones is not very clear. However, in order to explain this straightforward domino reaction, a reasonable possibility is shown in Scheme 1. At first isatin condensed with arylamine to give 3-*N*-aryliminoisatin (**A**) in the presence of acetic acid. Secondly isatin reacted with acetone resulting in isatylidene acetone (**B**) under the catalysis of acetic acid. Thirdly the nucleophilic addition of active methyl group of intermediate (**B**) to the imino group of intermediate (**A**) gave adduct (**C**). Then the intramolecular nucleophilic addition of amino group to the butene-1,4-dione unit in adduct (**C**) produced the final spiro compound **1**. The reaction of the previously prepared 3-*N*-*p*-methylphenyliminoisatin (**A**) with isatylidene acetone (**B**) or its undehydrated precursor 3-hydroxy-3-acetonylisatin in acetic acid at room temperature for several hours gave the expected spiro compound **1e** in moderate yield. This result gives a strong support to our above proposed reaction mechanism.

In conclusion, we have described a new one-pot sequential reaction of arylamines, acetone, and isatins, and found an efficient procedure for the synthesis of spiro[indoline-3,5′-pyrroline]-2,3′-dione. The reaction mechanism was briefly discussed. Prominent among the advantages of this new method are operational simplicity, good yields of products in short reaction times, and easy work-up procedures. Further expansion of the reaction scope and synthetic applications of this methodology are in progress in our laboratory.

Acknowledgments

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Supplementary data

Supplementary data (crystallographic data **1e** (CCDC has been deposited at the Cambridge Crystallographic Database Centre) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.05.023.

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22. *General procedure for the one-pot reactions of arylamines, acetone, and isatins:* A mixture of an arylamine (2.0 mmol) and isatin (4.0 mmol) in 10.0 mL acetic acid was stirred at room temperature for 2 h. Then acetone (5.0 mL) was added. The reaction mixture was stirred at room temperature for another 2–3 h. After adding water (30 mL), the resulting precipitate was collected by filtration and washed with a small portion of cold ethanol to give pure product for analysis.
Compound 1a: white solid, 70%, m.p. 238–241 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.50 (s, 1H, NH), 10.31 (s, 1H, NH), 7.62 (d, J = 7.2 Hz, 1H, ArH), 7.52–7.51 (m, 1H, ArH), 7.23 (t, J = 7.2 Hz, 1H, ArH), 7.15–7.10 (m, 2H, ArH), 6.97–6.93 (m, 3H, ArH), 6.74 (d, J = 7.2 Hz, 1H, ArH), 6.68–6.65 (m, 3H, ArH), 5.08 (d, J = 3.0 Hz, 1H, CH), 3.61 (s, 3H, OCH_3), 3.45 (br, 1H, CH), 2.79 (d, J = 18.0 Hz, 1H, CH), 2.68 (d, J = 18.0 Hz, 1H, CH); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 209.3, 199.7, 191.3, 182.7, 180.8, 178.8, 175.7, 156.8, 143.3, 142.5, 135.7, 129.7, 128.4, 127.9, 126.6, 126.2, 124.6, 124.4, 122.3, 121.1, 113.9, 110.1, 109.1, 86.9, 69.3, 66.9, 55.0, 46.5; IR (KBr) υ: 3184, 3084, 3033, 2900, 2837, 1762, 1712, 1620, 1510, 1469, 1331, 1289, 1243, 1195, 1124, 1031, 982, 940, 834, 776 cm^{-1}; MS (m/z): 438.31 ([M–H]$^-$, 100%); HRMS (ESI) Calcd for $C_{26}H_{20}N_3O_4$ ([M–H]$^-$): 438.1459. Found: 438.1460.
Compound 1b: white solid, 78%, m.p. 262–263 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.41 (s, 1H, NH), 10.21 (s, 1H, NH), 7.34 (s, 1H, ArH), 7.27 (br s, 1H, ArH), 7.04 (d, J = 7.8 Hz, 1H, ArH), 6.91–6.90 (m, 3H, ArH), 6.66–6.64 (m, 2H, ArH), 6.61 (d, J = 7.8 Hz, 1H, ArH), 6.58 (d, J = 7.8 Hz, 1H, ArH), 5.02 (d, J = 4.2 Hz, 1H, CH), 3.62 (s, 3H, OCH_3), 3.46 (br, 1H, CH), 2.77 (d, J = 18.0 Hz, 1H, CH), 2.67 (d, J = 18.0 Hz, 1H, CH), 2.35 (s, 3H, CH_3), 2.26 (s, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 209.2, 178.8, 175.7, 156.5, 140.9, 140.0, 136.1, 131.2, 129.9, 129.6, 18.8, 128.0, 126.2, 125.3, 124.8, 113.8, 109.9, 108.8, 69.2, 66.8, 55.0, 46.7, 20.8, 20.6; IR (KBr) υ: 3164, 3031, 2859, 1762, 1708, 1625, 1510, 1490, 1326, 1243, 1126, 1033, 815 cm^{-1}; MS (m/z): 466.29 ([M–H]$^-$, 100%); HRMS (ESI) Calcd for $C_{28}H_{24}N_3O_4$ ([M–H]$^-$): 466.1772. Found: 466.1772.
Compound 1e: white solid, 62%, m.p. 232–235 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.52 (s, 1H, NH), 10.33 (s, 1H, NH), 7.64 (d, J = 7.2 Hz, 1H, ArH), 7.53 (d, J = 6.6 Hz, 1H, ArH), 7.26 (t, J = 7.2 Hz, 1H, ArH), 7.17–7.12 (m, 2H, ArH), 6.96 (t, J = 7.2 Hz, 1H, ArH), 6.92–6.91 (m, 2H, ArH), 6.88–6.86 (m, 2H, ArH), 6.75 (d, J = 7.8 Hz, 1H, ArH), 6.71 (d, J = 7.8 Hz, 1H, ArH), 5.12–5.11 (m, 1H, CH), 3.50 (s, 1H, CH), 2.81 (d, J = 18.0 Hz, 1H, CH), 2.66 (d, J = 18.0 Hz, 1H, CH), 2.13 (s, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 209.0, 178.4, 175.7, 143.4, 142.4, 140.7, 134.0, 129.8, 129.3, 128.7, 127.9, 126.1, 124.6, 124.5, 123.9, 122.4, 121.1, 110.2, 109.2, 69.1, 66.4, 46.5, 20.3; IR (KBr) υ: 3347, 3056, 2922, 1761, 1719, 1621, 1512, 1469, 1393, 1328, 1284, 1252, 1230, 1192, 1114, 1020, 978, 928, 901, 830, 748 cm^{-1}; MS (m/z): 422.25 ([M–H]$^-$, 100%); HRMS (ESI) Calcd for $C_{26}H_{20}N_3O_3$ ([M–H]$^-$): 422.1510. Found: 422.1504.
Compound 1j: white solid, 52%, m.p. 248–251 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.54 (s, 1H, NH), 10.40 (s, 1H, NH), 7.62–7.61 (m, 1H, ArH), 7.43–7.42 (m, 1H, ArH), 7.28 (br s, 1H, ArH), 7.17–7.10 (m, 4H, ArH), 6.87 (br s, 3H, ArH), 6.74–6.70 (m, 2H, ArH), 5.13 (s, 1H, CH), 3.67 (s, 1H, CH), 2.88 (d, J = 18.0 Hz, 1H, CH), 2.78 (d, J = 18.0 Hz, 1H, CH); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 208.7, 178.0, 175.7, 143.3, 142.3, 130.0, 128.7, 128.6, 128.5, 127.9, 125.4, 124.6, 124.5, 122.6, 121.1, 110.4, 109.2, 69.2, 66.1, 46.5; IR (KBr) υ: 3345, 1762, 1717, 1622, 1490, 1469, 1391, 1329, 1285, 1252, 1196, 1090, 1012, 978, 930, 900, 841 cm^{-1}; MS (m/z): 442.25 ([M–H]$^-$, 100%); HRMS (ESI) Calcd for $C_{25}H_{17}ClN_3O_3$ ([M–H]$^-$): 442.0964. Found: 442.0958.