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# Efficient synthesis of imidazo[1,2-*a*]pyridin-3(2*H*)-ones

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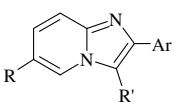
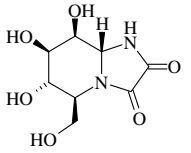
**Abstract**—2-Aminopyridines react with diaroylacetylenes to produce imidazo[1,2-*a*]pyridin-3(2*H*)-ones in good to excellent yields.


Imidazo[1,2-*a*]pyridines, fused bicyclic 5–6 heterocycles with one ring junction nitrogen atom and one extra nitrogen atom in the five-membered ring, are of interest because of the occurrence of their saturated and partially saturated derivatives in biologically active compounds.[1] Derivatives containing the imidazo[1,2-*a*]-pyridine ring system have been shown to possess a broad range of useful pharmacological activities, including antibacterial, antifungal, anthelmintic, antiviral, antiprotozoal, antiinflammatory, anticonvulsant, anxiolytic (e.g., Alpidem, **1**; Fig. 1), hypnotic (e.g., Zolpidem, **2**; Fig. 1), gastrointestinal, antiulcer (e.g., Zolmidine, **3**; Fig. 1), and immunomodulatory (e.g., Kifunensine, **4**; Fig. 1) activities.[1–4] Furthermore, some examples have been claimed to be cardiotonics, blood platelet aggregation inhibitors, acetylcholinesterase inhibitors,[1] cyclin dependent kinase inhibitors,[5] gastric $H^+/K^+$-ATPase inhibitors,[6] potential agents for imaging β-amyloids in Alzheimer's disease,[7] antagonists and agonists of the bradykinin B-2 receptor,[8] angiotensin II antagonists,[1] 5-$HT_3$ antagonists,[9] and potential inhibitors of UV-induced keratinocytes apoptosis.[10]

So far, several synthetic methods have been reported for the preparation of imidazo[1,2-*a*]pyridine ring systems: (i) in the most common synthetic methods the five-membered ring is constructed by condensation of 2-aminopyridines with α-haloketones or α-haloaldehydes, but this method has also been successful using other 1,2-dielectrophilic compounds such as α-ketohydroximoyl or α-ketohydrazidoyl chlorides, α-haloacyl cyanides, dicyano epoxides, α-epoxyketones or α-epoxyaldehydes, 1,2-diols, α-dicarbonyl compounds and 1,2-dihaloethanes; (ii) construction of the six-membered ring, however, no single procedure of wide applicability has emerged and the sequences reported are largely divided into annulation of imidazoles or reaction of cyclic ketene aminals; and (iii) formation of both rings.[1,3,4,9–11]




Alpidem, **1** [R = Cl; R' = $CH_2CON(CH_2CH_2CH_3)_2$; Ar = 4-$ClC_6H_4$]
Zolpidem, **2** [R = $CH_3$; R' = $CH_2CON(CH_3)_2$; Ar = 4-$CH_3C_6H_4$]
Zolmidine, **3** [R = R' = H; Ar = 4-$CH_3SO_2C_6H_4$]




Kifunensine, **4**

**Figure 1.** Examples of pharmacologically important imidazo[1,2-*a*]pyridines.

*Keywords*: 2-Aminopyridines; Diaroylacetylenes; Imidazo[1,2-*a*]pyridine-3(2*H*)-ones.
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As part of our ongoing program to develop efficient methods for the preparation of biologically interesting compounds, in this Letter we report a simple and efficient synthesis of imidazo[1,2-*a*]pyridin-3(2*H*)-ones. Thus, 2-aminopyridines **5** and diaroylacetylenes **6** undergo a smooth 1:1 addition reaction to produce 1,4-diaryl-2-(2-pyridylamino)-2-butene-1,4-diones **7**, which cyclize to 2-(2-oxo-2-arylethyl)-2-arylimidazo[1,2-*a*]pyridin-3(2*H*)-ones **8a**–**i** in 94–98% yields (Scheme 1).

The reactions were carried out by first mixing the 2-aminopyridine **5** and the diaroylacetylene **6** in dry $CH_2Cl_2$, and allowing the reaction to proceed at ambient temperature for a few hours. The $^1H$ NMR analysis of the reaction mixtures clearly indicated formation of the 1,4-diaryl-2-(2-pyridylamino)-2-butene-1,4-diones **7** in nearly quantitative yields. Structure **7a** was assigned to the isolated product on the basis of elemental analysis and high-field $^1H$ and $^{13}C$ NMR, IR and mass spectrometric data.[12] Then a solution of pyridine derivative **7** in toluene was refluxed for 6 h to produce functionalized imidazo[1,2-*a*]pyridin-3(2*H*)-one **8** in good to excellent yields. Any product other than **8** could not be detected by NMR spectroscopy.[13]

The structures of the isolated products **8a**–**i** were corroborated by their elemental analyses and IR, $^1H$ and $^{13}C$ NMR spectroscopy. The mass spectrum of **8a** displayed the molecular ion ($M^+$) peak at *m*/*z* 328. The $^1H$ NMR spectrum of **8a** exhibited an AB system ($\delta = 3.87$ and 4.22 ppm; $^2J_{HH} = 17.8$ Hz) arising from the two diastereotopic methylene protons, along with characteristic multiplets for the four protons of the electron-rich diene moiety of the six-membered ring, as well as characteristic multiplets with appropriate chemical shifts and coupling constants for the ten protons of the two phenyl groups. The proton decoupled $^{13}C$ NMR spectrum of **8a** showed 17 distinct resonances in agreement with the proposed structure. Partial assignments of these resonances are given.[13] Single-crystal X-ray analysis conclusively confirmed the structure of the isolated products. An ORTEP diagram of **8a** is shown in Figure 2.[14]

Mechanistically, it is reasonable to assume that nucleophilic addition of the pyridine *N*-atom to the carbonyl group yields imidazo[1,2-*a*]pyridine intermediate **9**. Migration of the aryl substituent to the adjacent α, β-unsaturated carbonyl group, which is facilitated by reformation of the carbonyl bond and proton transfer from the iminium moiety, produces the functionalized imidazo[1,2-*a*]pyridin-3(2*H*)-one **8** (Scheme 2).

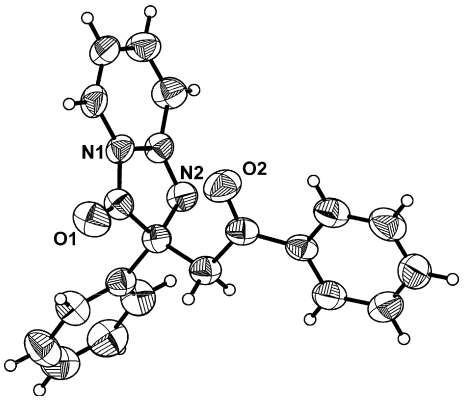
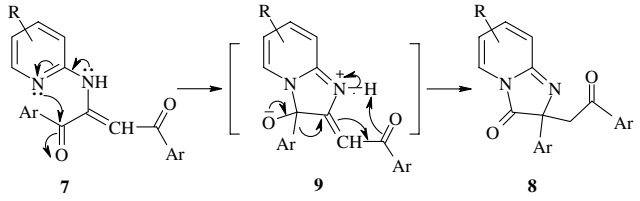
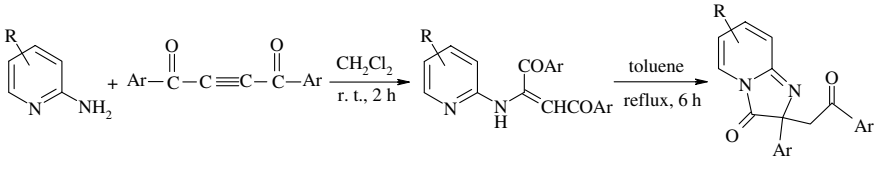



**Figure 2.** Molecular structure of **8a**, with 50% probability displacement ellipsoids, H atoms with arbitrary radii.



**Scheme 2.**



**5** **6** **7** **8**

| **5** | R |
|---|---|
| **a** | H |
| **b** | 3-$CH_3$ |
| **c** | 4-$CH_3$ |
| **d** | 5-$CH_3$ |

| **6** | Ar |
|---|---|
| **a** | $C_6H_5$ |
| **b** | 4-$CH_3C_6H_4$ |
| **c** | 2,5-$(CH_3)_2C_6H_3$ |

| **8** | R | Ar | % Yield[a] |
|---|---|---|---|
| **a** | H | $C_6H_5$ | 98 |
| **b** | H | 4-$CH_3C_6H_4$ | 94 |
| **c** | H | 2,5-$(CH_3)_2C_6H_3$ | 96 |
| **d** | 8-$CH_3$ | $C_6H_5$ | 97 |
| **e** | 8-$CH_3$ | 4-$CH_3C_6H_4$ | 95 |
| **f** | 8-$CH_3$ | 2,5-$(CH_3)_2C_6H_3$ | 96 |
| **g** | 7-$CH_3$ | $C_6H_5$ | 94 |
| **h** | 7-$CH_3$ | 2,5-$(CH_3)_2C_6H_3$ | 94 |
| **i** | 6-$CH_3$ | $C_6H_5$ | 95 |

[a] isolated yields

**Scheme 1.**

In conclusion, we have developed a simple and efficient method for the preparation of imidazo[1,2-*a*]pyridin-3(2*H*)-ones of potential synthetic and pharmacological interest. This method carries the advantage that not only is the reaction performed under neutral conditions, but also the substances can be mixed without any modification. The simplicity of this procedure makes it an interesting alternative to other approaches.

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12. The procedure for the preparation of 1,4-diphenyl-2-(2-pyridylamino)-2-butene-1,4-dione **7a** is described. To a magnetically stirred solution of 2-aminopyridine **5a** (0.188 g, 2 mmol) in dry $CH_2Cl_2$ (5 mL) was added dropwise a solution of dibenzoylacetylene **6a** (0.468 g, 2 mmol) in dry $CH_2Cl_2$ (2 mL) at 25 °C for 10 min. The reaction mixture was stirred for 2 h. Then the solvent was removed and the solid residue was recrystallized from EtOAc as red crystals, mp 145–147 °C, yield 0.65 g, 99%. IR (KBr) ($\nu_{max}$/cm$^{-1}$): 3430 (NH), 1639 (C=O), 1570, 1520, 1434, 1384, 1320, 1241, 1199, 1146, 1038, 982, 860, 740, 695. EI-MS, *m*/*z* (%): 328 ($M^+$, 16), 299 (9), 251 (19), 223 (29), 207 (37), 121 (65), 105 (83), 78 (100), 57 (34). Anal. Calcd for $C_{21}H_{16}N_2O_2$ (328.37): C, 76.81; H, 4.91; N, 8.53. Found: C, 76.5; H, 5.0; N, 8.3. $^1$H NMR (500.1 MHz, $CDCl_3$): $\delta$ 6.00 (1H, t, $J = 6.7$ Hz, CH), 6.58 (1H, d, $J = 9.7$ Hz, CH), 6.90 (1H, dd, $J = 9.6$ Hz and $J = 6.5$ Hz, CH), 7.00 (1H, s, CH), 7.21 (1H, t, $J = 7.2$ Hz, CH), 7.27 (2H, dd, $J = 7.3$ Hz and $J = 7.7$ Hz, 2CH), 7.30–7.34 (1H, d, $J = 7.3$ Hz, CH and 1H, br, NH), 7.43 (2H, t, $J = 7.6$ Hz, 2CH), 7.54 (1H, t, $J = 6.4$ Hz, CH), 7.55 (2H, d, $J = 7.4$ Hz, 2CH), 7.85 (2H, d, $J = 7.6$ Hz, 2CH). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$ 99.89 ($CH_{vinyl}$), 101.33, 108.04, 119.17, 124.95, 125.22, 127.92, 128.14, 128.21, 128.55 and 133.19 (10CH), 136.34 and 138.00 ($2C_{ipso}$, PhCO), 140.43 (C–N), 154.71 (N–C=N), 165.09 and 190.58 (2C=O).
13. *General procedure for the preparation of imidazo[1,2-a]pyridines* **8a**–**i** *exemplified by 2-(2-oxo-2-phenylethyl)-2-phenylimidazo[1,2-a]pyridine-3(2H)-one* ***8a***: A solution of **7a** (1 mmol) in toluene (20 mL) was refluxed for 6 h. The solvent was removed, and the residue was crystallized from EtOAc–*n*-hexane (2:1) to afford **8a** as yellow crystals, mp 151–152 °C, yield 0.32 g, 98%. IR (KBr) ($\nu_{max}$/cm$^{-1}$): 1744 and 1680 (C=O), 1649, 1572, 1531, 1487, 1442, 1335, 1229, 1180, 996, 754, 694. EI-MS, *m*/*z* (%): 328 ($M^+$, 6), 301 (2), 195 (14), 181 (16), 105 (100), 77 (27), 52 (21). Anal. Calcd for $C_{21}H_{16}N_2O_2$ (328.37): C, 76.81; H, 4.91; N, 8.53. Found: C, 76.6; H, 4.7; N, 8.2. $^1$H NMR (500.1 MHz, $CDCl_3$): $\delta$ 3.87 and 4.22 (2H, 2d, AB system, $^2J = 17.8$ Hz, $CH_AH_B$), 6.05 (1H, t, $J = 6.7$ Hz, CH), 6.73 (1H, d, $J = 9.6$ Hz, CH), 7.02 (1H, dd, $J = 9.6$ Hz and $J = 6.3$ Hz, CH), 7.34 (1H, t, $J = 7.3$ Hz, CH), 7.39 (2H, dd, $J = 7.8$ Hz and $J = 7.1$ Hz, 2CH), 7.40 (2H, dd, $J = 7.5$ Hz and $J = 7.8$ Hz, 2CH), 7.44 (1H, d, $J = 7.2$ Hz, CH), 7.53 (1H, t, $J = 7.4$ Hz, CH), 7.80 (2H, d, $J = 7.7$ Hz, 2CH), 7.87 (2H, dd, $J = 8.0$ Hz and $J = 0.8$ Hz, 2CH). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$ 50.30 ($CH_2$), 71.47 (C), 107.80 (CH-6), 119.09 (CH-8), 125.08 (CH-5), 126.15 and 128.13 (2CH), 128.24 ($CH_{para}$, Ph), 128.52 and 128.72 (2CH), 133.44 ($CH_{para}$, PhCO), 135.77 ($C_{ipso}$, Ph), 137.18 (CH-7), 138.10 ($C_{ipso}$, PhCO), 157.32 (N–C=N), 181.35 (C=O, amide), 195.75 (C=O, ketone). *8-Methyl-2-(2-oxo-2-phenylethyl)-2-phenylimidazo[1,2-a]pyridine-3(2H)-one* **8d**: Yellow crystals, mp 160–162 °C, yield 0.33 g, 97%. IR (KBr) ($\nu_{max}$/cm$^{-1}$): 1730 and 1672 (C=O), 1611, 1467, 1417, 1214, 1074, 755, 685. EI-MS, *m*/*z* (%): 342 ($M^+$, 6), 316 (2), 223 (29), 209 (38), 195 (29), 105 (100), 92 (66), 77 (79), 65 (22), 51 (17). Anal. Calcd for $C_{22}H_{18}N_2O_2$ (342.40): C, 77.17; H, 5.30; N, 8.18. Found: C, 77.2; H, 5.1; N, 8.2. $^1$H NMR (500.1 MHz, $CDCl_3$): $\delta$ 2.20 (3H, s, $CH_3$), 3.88 and 4.28 (2 H, 2d, AB system, $^2J = 17.8$ Hz, $CH_AH_B$), 5.98 (1H, t, $J = 6.7$ Hz, CH), 6.79 (1H, d, $J = 5.7$ Hz, CH), 7.30–7.34 (2H, m,2CH), 7.38 (2H, t, $J = 7.6$ Hz, 2CH), 7.39 (2H, t, $J = 7.7$ Hz, 2CH), 7.52 (1H, dd, $J = 7.5$ Hz and $J = 7.2$ Hz, CH), 7.83 (2H, d, $J = 7.6$ Hz, 2CH), 7.87 (2H, d, $J = 7.6$ Hz, 2CH). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$ 16.37 ($CH_3$), 50.23 ($CH_2$), 71.84 (C), 107.94 (CH-6), 122.69 (CH-5), 126.26 ($CH_3$-*C*), 126.27 and 128.22 (2CH), 128.26 ($CH_{para}$, Ph), 128.58 and 128.74 (2CH), 133.43 ($CH_{para}$, PhCO), 133.62 ($C_{ipso}$, Ph), 136.04 (CH-7), 138.64 ($C_{ipso}$, PhCO), 158.33 (N–C=N), 182.09 (C=O, amide), 195.88 (C=O, ketone). *2-(2,5-Dimethylphenyl)-2-[2-(2,5-dimethylphenyl)-2-oxoethyl]-8-methylimidazo-[1,2-a]pyridine-3(2H)-one* **8f**: Yellow crystals, mp 142–144 °C, yield

0.38 g, 96%. IR (KBr) ($\nu_{max}$/cm$^{-1}$): 1733 and 1676 (C=O), 1636, 1573, 1487, 1331, 809, 736. EI-MS, *m*/*z* (%): 398 ($M^+$, 4), 370 (1), 355 (2), 265 (21), 251 (19), 237 (100), 223 (20), 133 (57), 105 (58), 92 (34), 77 (15), 65 (17). Anal. Calcd for $C_{26}H_{26}N_2O_2$ (398.50): C, 78.36; H, 6.58; N, 7.03. Found: C, 78.5; H, 6.3; N, 6.8. $^1$H NMR (500.1 MHz, $CDCl_3$): $\delta$ 2.12 (3H, br s, $CH_3$), 2.32, 2.34, 2.36 and 2.73 (12H, 4s, $4CH_3$), 3.78 and 4.26 (2H, 2d, AB system, $^2J = 16.6$ Hz, $CH_AH_B$), 5.95 (1H, br t, CH), 6.72 (1H, br d, CH), 7.03 (1H, d, $J = 7.4$ Hz, CH), 7.08 (1H, d, $J = 7.7$ Hz, CH), 7.11 (1H, d, $J = 7.6$ Hz, CH), 7.15 (1H, d, $J = 7.7$ Hz, CH), 7.37 (1H, d, $J = 5.4$ Hz, CH), 7.46 (1H, br s, CH), 7.48 (1H, s, CH). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$ 16.07, 20.45, 20.87, 21.12 and 22.07 ($5CH_3$), 50.05 ($CH_2$), 74.76 (C), 107.76 (CH-6), 122.45 (CH-5), 126.85 and 128.53 (2CH), 128.71 ($CH_3$-*C*8), 129.21, 131.64, 132.06, 132.73 and 133.14 (5CH), 134.80, 134.95, 135.02, 135.10 and 135.44 ($4CH_3$-*C* and $C_{ipso}$, Ar), 137.62 ($C_{ipso}$, ArCO), 157.38 (N–C=N), 182.59 (C=O, amide), 200.40 (C=O, ketone). *7-Methyl-2-(2-oxo-2-phenylethyl)-2-phenylimidazo[1,2-a]pyridine-3(2H)-one* **8g**: Yellow crystals, mp 120–123 °C, yield 0.32 g, 94%. IR (KBr) ($\nu_{max}$/cm$^{-1}$): 1732 and 1674 (C=O), 1647, 1573, 1480, 1436, 1350, 1316, 1219, 1177, 993, 750, 700. EI-MS, *m*/*z* (%): 342 ($M^+$, 1), 298 (2), 237 (4), 211 (38), 195 (32), 105 (66), 77 (84), 61 (100), 43 (86). Anal. Calcd for $C_{22}H_{18}N_2O_2$ (342.40): C, 77.17; H, 5.30; N, 8.18. Found: C, 76.9; H, 5.5; N, 8.0. $^1$H NMR (500.1 MHz, $CDCl_3$): $\delta$ 2.09 (3H, s, $CH_3$), 3.81 and 4.15 (2H, 2d, AB system, $^2J = 17.8$ Hz, $CH_AH_B$), 5.83 (1H, d, $J = 7.2$ Hz, CH), 6.44 (1H, s, CH), 7.30 (2H, t, $J = 7.2$ Hz, 2CH), 7.34 (2H, t, $J = 7.6$ Hz, 2CH), 7.35 (2H, t, $J = 7.5$ Hz, 2CH), 7.48 (1H, t, $J = 7.3$ Hz, CH), 7.77 (2H, d, $J = 7.6$ Hz, 2CH), 7.83 (2H, d, $J = 7.7$ Hz, 2CH). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$ 22.03 ($CH_3$), 50.11 ($CH_2$), 71.72 (C), 111.04 (CH-6), 116.16 (CH-8), 123.97 (CH-5), 126.17 (CH), 128.11 ($CH_{para}$, Ph), 128.13, 128.50 and 128.66 (3CH), 133.35 ($CH_{para}$, PhCO), 136.00 ($C_{ipso}$, Ph), 138.67 ($C_{ipso}$, PhCO), 148.34 ($CH_3$-*C*), 157.50 (N–C=N), 181.39 (C=O, amide), 195.89 (C=O, ketone).

14. *Selected X-ray crystallographic data for compound* **8a**: $C_{21}H_{16}N_2O_2$, monoclinic, space group = $P2_1/c$ (No. 14), $a = 6.6014(8)$ Å, $b = 20.927(2)$ Å, $c = 12.4508(19)$ Å, $\beta = 101.495(14)°$, $V = 1685.5(4)$ Å$^3$, $T = 290(2)$ K, $Z = 4$, $D_{calcd} = 1.294$ g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 0.084 mm$^{-1}$, 12,763 reflections measured, 4041 unique reflections ($R_{int} = 0.0333$), 2301 observed reflections, final $R_1 = 0.0422$, $wR_2 = 0.1058$ and for all data $R_1 = 0.0723$, $wR_2 = 0.1119$. CCDC 637470 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via the internet (http://www.ccdc.cam.ac.uk/data_request/cif), e-mail: (data_request@ccdc.cam.ac.uk), or fax: (+44-1223-336033).