Synthesis and Spectroscopic Properties of New Fluorescent 3,6-Diaryl-4-phenyl-2-pyridone Derivatives

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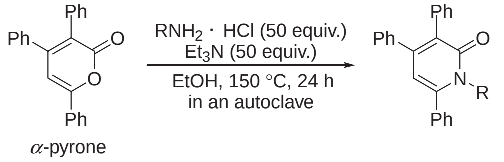
Novel fluorescent 3,6-diaryl-4-phenyl-2-pyridone derivatives were synthesized and their fluorescent properties were investigated. These compounds emit intense brilliant blue fluorescence only in the solid state, not in solution. An electron-donating substituent on the 6-phenyl group caused a red-shift in fluorescence maxima.

Fluorescent organic molecules have garnered much interest for a variety of applications including their use as fluorescent probes and in optoelectronics due to their spectroscopic properties.[1–3] Thus, a new series of fluorophores have been developed.[4–6] Fluorophores that show fluorescence in the solid state are particularly useful in photofunctional applications, such as fluorescent pigments used in electroluminescent devices.[7] We previously reported on 6-aryl-3,4-diphenyl-α-pyrone derivatives that are potential candidates for these applications, because they show intense blue to orange (λ_{flu}: 470–570 nm) fluorescence only in the solid state.[8] To intensify the brilliance and color purity of blue-emitters the present study focused on the pyridone framework,[9] aza-analogs of pyrones, for the synthesis of the novel fluorophores. The replacement, in the ring, of oxygen with nitrogen changes the contribution of the resonance structures, causing blue-shift. This paper describes synthesis of pyridone derivatives and their unique fluorescent properties. Since the desired pyridones are expected to emit in the solid state in a similar manner with pyrones,[8] the present study would be basic research directly connecting with practical fluorophores.

The desired N-alkylated 3,4,6-triphenyl-2-pyridones were readily synthesized, with good yields, by reacting the corresponding pyrones with amines (Table 1). The absorption spectra of the pyridones were measured in dichloromethane. The absorption maxima of all compounds occurred at nearly the same wavelength approximately 340 nm. In solution, the pyridone derivatives did not emit fluorescence, which was consistent with previously published results for α-pyrones.[8] As discussed in our previous work,[8] the phenomenon would be explained by rotational freedom of the 6-phenyl group. Although X-ray structure analysis should be performed, the phenyl ring would be fixed in the solid state by molecular packing and the path of fluorescence was thus increased. On the other hand, the free rotation of the phenyl group would be allowed in solution. However, the pyridones emitted an intense blue fluorescence in the solid state, and, as expected, the fluorescent maxima were remarkably blue-shifted compared with the maxima of pyrones. The emission of the shorter wavelength makes pyridones promising material as blue emitters. Relative fluorescent intensities of the pyridones were evaluated by comparing them with that of pyrene, which is a well-known, representative blue-fluorescent pigment. The intensities of the pyridones, with the exception of **1a** and **1g**, were stronger than that of pyrene; **1e** and **1c** emitted a considerably stronger fluorescence (Figure 1).

Because pyridone **1e** exhibited the strongest blue fluorescent intensity, the influence of substituents of the phenyl ring at the 3- and 6-positions on fluorescent properties of pyridones

Table 1. Synthesis of pyridones and their spectroscopic properties



Entry	R	Pyridone	Yield/%	λ_{abs}/nm[a]	λ_{flu}/nm
1	Me	**1a**	89	340	441
2	Et	**1b**	82	337	437
3	*n*-Pr	**1c**	74	339	432
4	*i*-Pr	**1d**	67	342	440
5	*n*-Bu	**1e**	79	339	439
6	*i*-Bu	**1f**	71	340	425
7	*sec*-Bu	**1g**	60	340	441

[a]In a solution of CH_2Cl_2 (1.0×10^{-4} M).

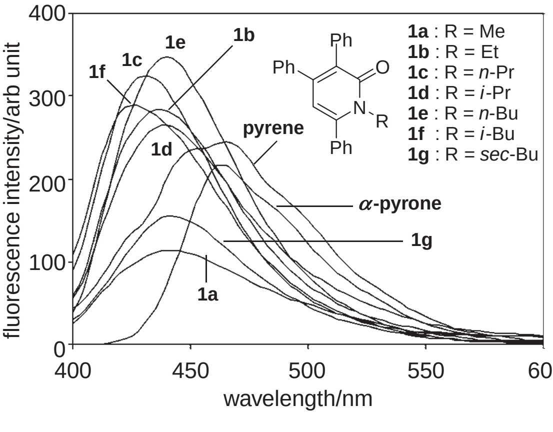
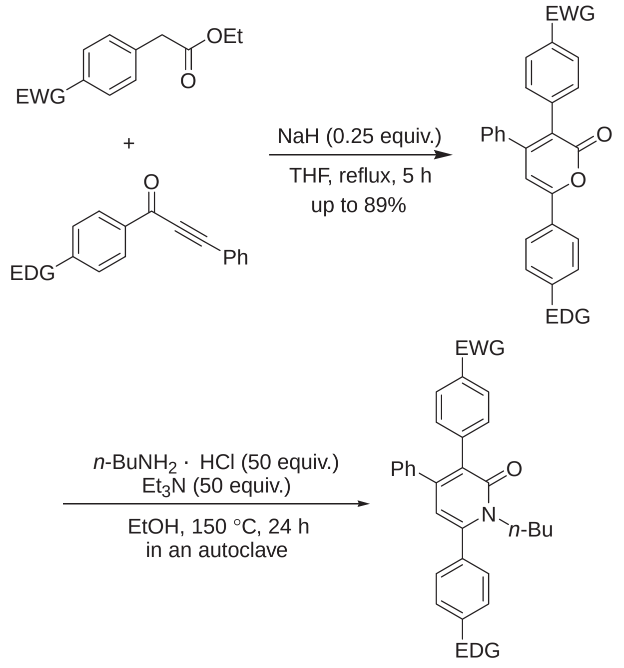


Figure 1. Comparison of fluorescence intensity of pyridones **1** with that of pyrene and α-pyrone at the powdered form.



Scheme 1. Synthesis of *N*-butylpyridones.

was investigated. To enhance intramolecular charge transfer, pyridones with electron-withdrawing groups at the para-position on the 3-substituted phenyl ring and electron-donating groups at the para-position on the 6-substituted phenyl ring were synthesized from the corresponding pyrone derivatives. The pyrones were prepared from ethyl arylacetates and aroylphenylacetylenes in the presence of a base, using modification of previously published methods.[10] Although stoichiometric amounts of base either sodium methoxide or sodium hydride were used in previous studies, this method led to poor yields of the desired pyrones. When various bases were evaluated for use in pyrone synthesis, sodium hydride was found to work well and to act as a catalyst in the reaction. The pyrones obtained were successfully converted to the corresponding N-butylated pyridones (Scheme 1). The yields of the last step (from pyrones to pyridones) and spectroscopic properties **2**–**9** are listed in Table 2.

Although the absorption maxima of pyridones **2**–**5** that had a methoxy group as the electron-donating group, were almost the same as those of the pyridones, the introduction of a dimethylamino group induced a slight red-shift. Fluorescent maxima of these compounds, especially, **6**–**9** that had dimethylamino groups showed a marked tendency to red-shift. The reason for the red-shift may be the presence of a strong electron-donating group that decreases the torsion angle of the pyridone plane and the aryl group at the 6-position.[8b,11] Pyridones **2**–**5** also emitted blue fluorescence only in the solid state, but the intensities were relatively weak compared with the mother pyridone **1e** (Table 2).

Table 2. Spectroscopic properties of *N*-butylpyridones

Entry	EDG	EWG	Pyridone	Yield/%	λ_{abs}/nm[a]	λ_{flu}/nm
1	OMe	H	**2**	82	340	434
2	OMe	Br	**3**	69	345	440
3	OMe	CF_3	**4**	70	346	437
4	OMe	CN	**5**	42	350	440
5	NMe_2	H	**6**	79	351	519
6	NMe_2	Br	**7**	95	355	483
7	NMe_2	CF_3	**8**	73	355	451
8	NMe_2	CN	**9**	52	365	547

[a] In a solution of CH_2Cl_2 (1.0×10^{-4} M).

In summary, novel fluorophores, 3,6-diaryl-4-phenyl-2-pyridone derivatives were synthesized and their spectroscopic properties were described. The compounds emitted intense blue fluorescence only in the solid state, not in solution. An electron-donating substituent on the 6-phenyl group caused a red-shift in fluorescence maxima. Although examination of the unusual fluorescent properties of the pyridones in the solid state by X-ray structure analyses should be performed in the near future, this paper describes the successful synthesis of new type of fluorophore, showing brilliant blue emission.

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