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# PROPERTIES OF THE KETO AMIDES FORMED BY AMINOLYSIS OF 3,7-DIARYLPYRANO[4,3-*c*]PYRAN-1,5-DIONE DERIVATIVES: A SOLID-STATE REACTION, CRYSTAL STRUCTURES, AND THERMAL ANALYSIS

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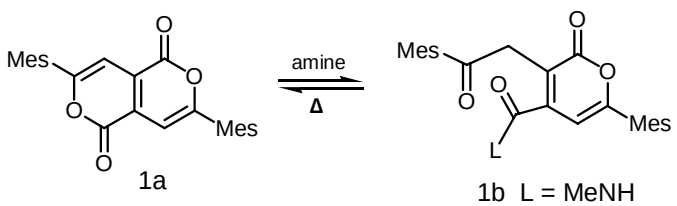
**Abstract** – Aminolysis of 3,7-diarylpyrano[4,3-*c*]pyran-1,5-dione derivatives gave keto amides, which upon heating returned back to the original compounds in the solid state. X-Ray crystallographic analysis of the keto amides showed proximate orientations of the ketone and the amide groups. TGA and DTA of the keto amides clarified a kind of solid-state reaction which occurred in appearance without melting, but microscopically proceeded via melting of the keto amides, structural change, and crystallization of the products.

Solid-state reactions are attracting a considerable attention, since they do not require disposal of solvents and often lead to pure products.[1] Color changes of solid materials have been a current interest in material science.[2] A variety of solid-state reactions (solvent-free reactions) have been reported. Reactions of amines with carbonyl compounds have been studied.[3] In a previous paper, we reported that aminolysis of 3,7-dimesitylpyrano[4,3-*c*]pyran-1,5-dione (**1a)** with $MeNH_2$ gave a keto amide (**1b)**, which returned back to **1a** in the solid state upon heating above 300 °C for 10 min.[4] In this paper we wish to report the properties of a series of keto amides (**1b** – **8b**) derived from fluorescent 3,7-diarylpyrano[4,3- *c*]pyran-1,5-diones (**1a** and **3a** – **8a**) .




1a
Mes = 2,4,6-$Me_3C_6H_2$

1b L = MeNH
2b L = $Me_2N$

Chart 1.

## RESULTS AND DISCUSSION

Keto amides (**2b** – **8b**) were prepared as follows. In order to change the amide moiety of **1b**, the compound (**1a**) was treated with $Me_2NH$ to give an *N*,*N*-dimethyl amide (**2b)**. One of the mesityl groups in **2b** seemed to affect steric effect for the neighboring ketone group. Subsequently, the mesityl groups in **2b** were replaced with phenyl groups, and a compound **(3a)**[5] was converted to an amide (**3b)** with $Me_2NH$**,** since aminolysis with $MeNH_2$ gave a ring tautomer (**A**) in the ring chain tautomerism. The amide (**3b**) was unstable, and returned back to **3a** during recrystallization from boiling EtOAc or

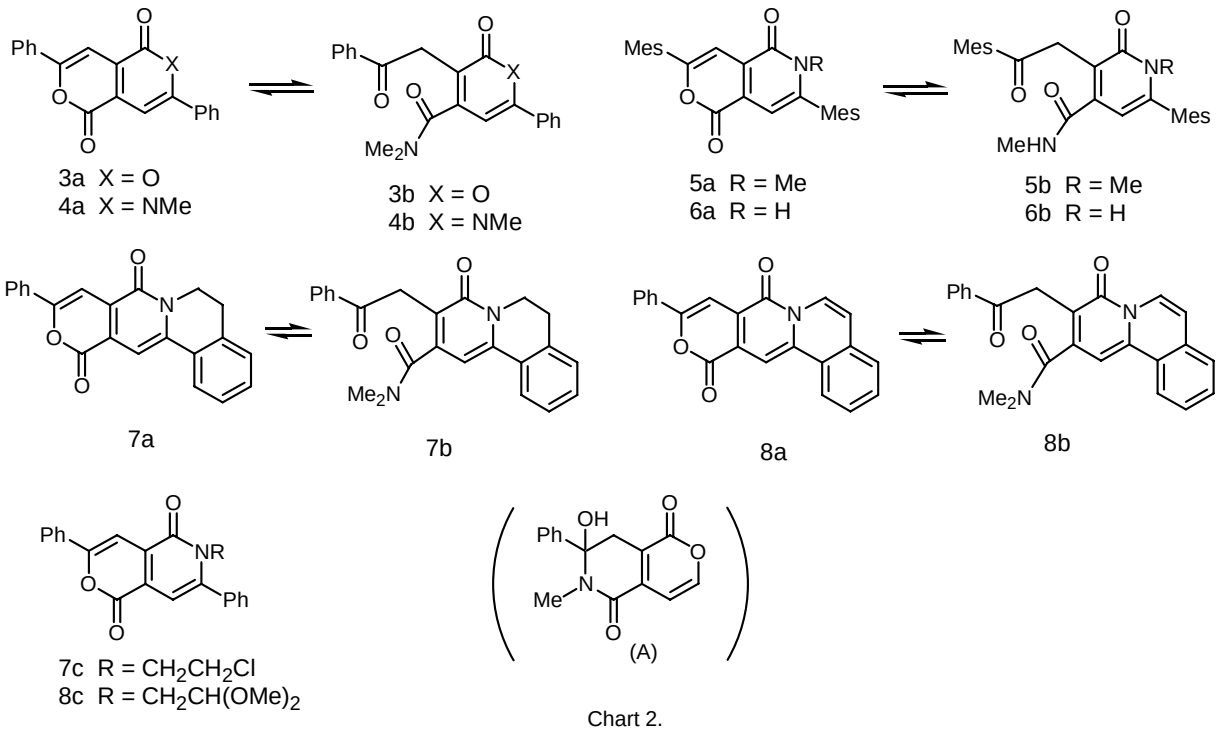



Chart 2.

during column chromatography. The mesityl groups in **1b** and **2b** would affect steric protection for the ketone groups. Similarly, a compound (**4a**)[4] was converted to an amide (**4b**)**,** which was thermally more stable than **3b**. On the other hand, a compound (**5a**)[4] was treated with $MeNH_2$ to give an amide (**5b**) bearing an *N*-methyl 2-pyridone ring. A compound (**6a**) was prepared from **1a** in very low yield (2.6%) by aminolysis with $NH_3$ followed by cyclization with $POCl_3$. Aminolysis of **6a** with $MeNH_2$ afforded an amide (**6b**) bearing a 2-pyridone ring. Each **5b** and **6b** gave a stable single crystal which was subjected to X-ray crystallographic analysis. We planned to prepare compounds (**7a** and **8a**) by fixing one of the benzene rings in **4a** with a methylene bridge or a double bond. Upon treating with $AlCl_3$, a compound (**7c**)[4] gave the compound (**7a**), which yielded an amide (**7b**) with $Me_2NH$. The compound (**7c**) was prepared from **3a** by aminolysis with 2-aminoethanol followed by treatment with $POCl_3$. On the other hand, a compound (**8c**) was prepared from **3a** by aminolysis with aminoacetaldehyde dimethyl

acetal followed by TFA treatment. Upon treating with $AlCl_3$, the compound (**8c**) afforded the compound (**8a**) bearing the extended π conjugation. Similarly, **8a** was converted to an amide (**8b**) with $Me_2NH$.
In the $^1H$ NMR spectra of **2b**, **5b** and **6b**, the signals of the methylene protons attached to mesitoyl groups appear as singlet (2H), whereas the signals of the methylene protons adjacent to the benzoyl groups in **3b**, **4b**, **7b**, and **8b** are very broad, or not observed perhaps due to the molecular movement.

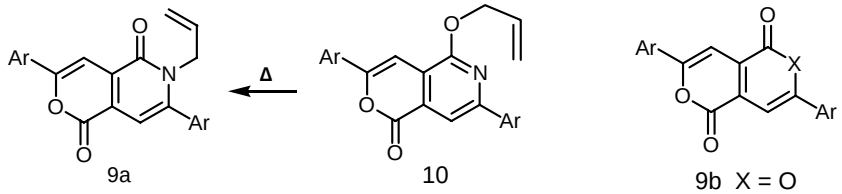



Chart 3.

Tautomerism between 2-pyridone and 2-hydroxypyridine has been well studied.[6] A crystal structure of a 4-subsutituted-2-pyridone has been reported.[7] A 2-pyridone form of **6b** was clarified by X-ray analysis, as described below. Lactam-lactim tautomerism has also been well studied. It was shown by absorption spectral data that **6a** existed in a lactam form. Furthermore, an equilibrium between a lactam (**9a**) bearing an *N*-allyl group and a lactim (**10**) with an *O*-allyl group was examined in order to compare their stability. In this experiment, a compound (**9b**)[4] bearing 2-methylphenyl groups was used as a starting compound. Upon aminolysis with allylamine followed by cyclization with $POCl_3$, **9b** gave the compound (**9a**, UV-VIS $\lambda_{max}$ 394 nm). On the other hand, **9b** was converted to **9c (**UV-VIS 395 nm) by aminolysis with $NH_3$ followed by treatment with $POCl_3$. The reaction of **9c** with allyl bromide in the presence of $Ag_2O$ afforded **10**, which showed the $\lambda_{max}$ at shorter wavelength (368 nm) relative to that of **9a**. Upon heating at 270° for 1 h, **10** underwent a sigmatropic reaction to give **9a** exclusively, indicating that **9a** was more stable than **10**. Accordingly, the compounds (**6a** and **9c**) exist in a stable lactam form.

## ABSORPTION AND FLUORESCENCE SPECTRA

Absorption and fluorescence spectral data of the compounds (**1a**, **2b**, and **3a,b** – **8a,b**) are summarized in Table 1. The compounds (**5a** and **6a**) exhibit their $\lambda_{max}$ at the same region, and the $\lambda_{max}$ of the compounds (**5b** and **6b**) are observed at almost the same region. These data are in line with the lactam form of **6a** and the 2-pyridone form of **6b**, respectively. The benzene rings in the compounds (**7a** and **7b**) are fixed with methylene bridges, and their $\lambda_{max}$ appear at longer wavelengths relative to those of the compounds (**4a** and **4b**), indicating the bathochromic shifts caused by the coplanar benzene rings, respectively. The compounds (**8a** and **8b**) have the extended π conjugation (-N-CH=CH-benzene ring), and exhibit the $\lambda_{max}$ at longer wavelengths relative to those of the compounds (**7a** and **7b**), indicating the bathochromic shifts due to the double bonds by 50 and 68 nm, respectively. The compounds (**1a** and **3a**

– **8a**) are fluorescent, and the $\lambda_{max}$ of fluorescence ($F_{max}$) are summarized in Table 1. The compound (**1a**) shows a large Stokes shift by 90 nm. The compound (**8b**) is also fluorescent and indicates $F_{max}$ at 445 nm.

Table 1. Absorption and Fluorescence Spectral Data of **1a**, **2b** and **3a,b** – **8a,b**

| Compounds | $\lambda_{max}$(nm) | $F_{max}$(nm) | Keto amides | $\lambda_{max}$(nm) |
|---|---|---|---|---|
| **1a** | 388 | 478 | **2b** | 316 |
| **3a** | 429 | 480 | **3b** | 340 |
| **4a** | 425 | 454 | **4b** | 323 |
| **5a** | 383 | 452 | **5b** | 324 |
| **6a** | 383 | 453 | **6b** | 323 |
| **7a** | 447 | 461 | **7b** | 351 |
| **8a** | 497 | 506 | **8b** | 419 |

## CRYSTAL STRUCTURES

X-Ray crystallographic analysis was carried out for **5b**, **6b** and **8b** in order to know the orientations of the aroyl and the amide moieties.[8] The ORTEP views of **5b**, **6b** and **8b** are shown in Figure 1 (a), (b), and (c), respectively. The bond distances of the carbonyl groups in **5b** [C(1)-O(1) 1.230(2) Å] and **8b** [1.232(3) Å ] are slightly shorter than that in **6b** [1.249(2) Å], but these data support that **6b** exists in a 2-pyridone form. The mesityl and 2-pyridone rings in **5b** and **6b** are twisted with respect to each other, and the torsion angle in **5b** [C(4)-C(5)-C(20)-C(21)] is 87.3°(2), and that in **6b** is 76.9°(2). The *N*-methyl amide carbonyl groups and the 2-pyridone rings in **5b** and **6b** are also twisted with respect to each other, and the torsion angle in **5b** [O(3)-C(18)-C(3)-C(2)] is 41.6° and that in **6b** is 41.4°, whereas the corresponding torsion angle in **8b** [O(3)-C(22)-C(3)-C(2)] is 70.4°. Due to these torsion, the ketonic carbonyl and the *N*-methyl amide carbonyl groups are brought close, and the distance between the ketonic oxygen O(2) and the amide carbonyl carbon C(18) in **5b** is 4.05 Å, and the corresponding distances in **6b** and **8b** are 3.33 and 3.50 Å, respectively. Interestingly, the distance between the methylene carbon C(7) and the amide carbonyl oxygen O(3) in **5b** is 3.02 Å as shown in Figure 1 (d), and the corresponding distances in **6b** and **8b** are 2.98 Å and 3.21 Å, respectively. Furthermore, the distance between one of the hydrogen atoms on C(7) and the amide carbonyl oxygen O(3) in **5b** is estimated to be 2.28 Å, and those in **6b** and **8b** are 2.37 and 2.60 Å, respectively. These distances are shorter than the sum of the van der Waals radii (H 1.20 and O 1.52 Å), suggesting the C-H···O interaction between the methylene hydrogen and the amide carbonyl oxygen O(3).[9] The proximate orientations of the ketonic and the

amide carbonyl groups in **5b**, **6b**, and **8b** are in line with the observed conversion to the original compounds (**5a**, **6a**, and **8a**),

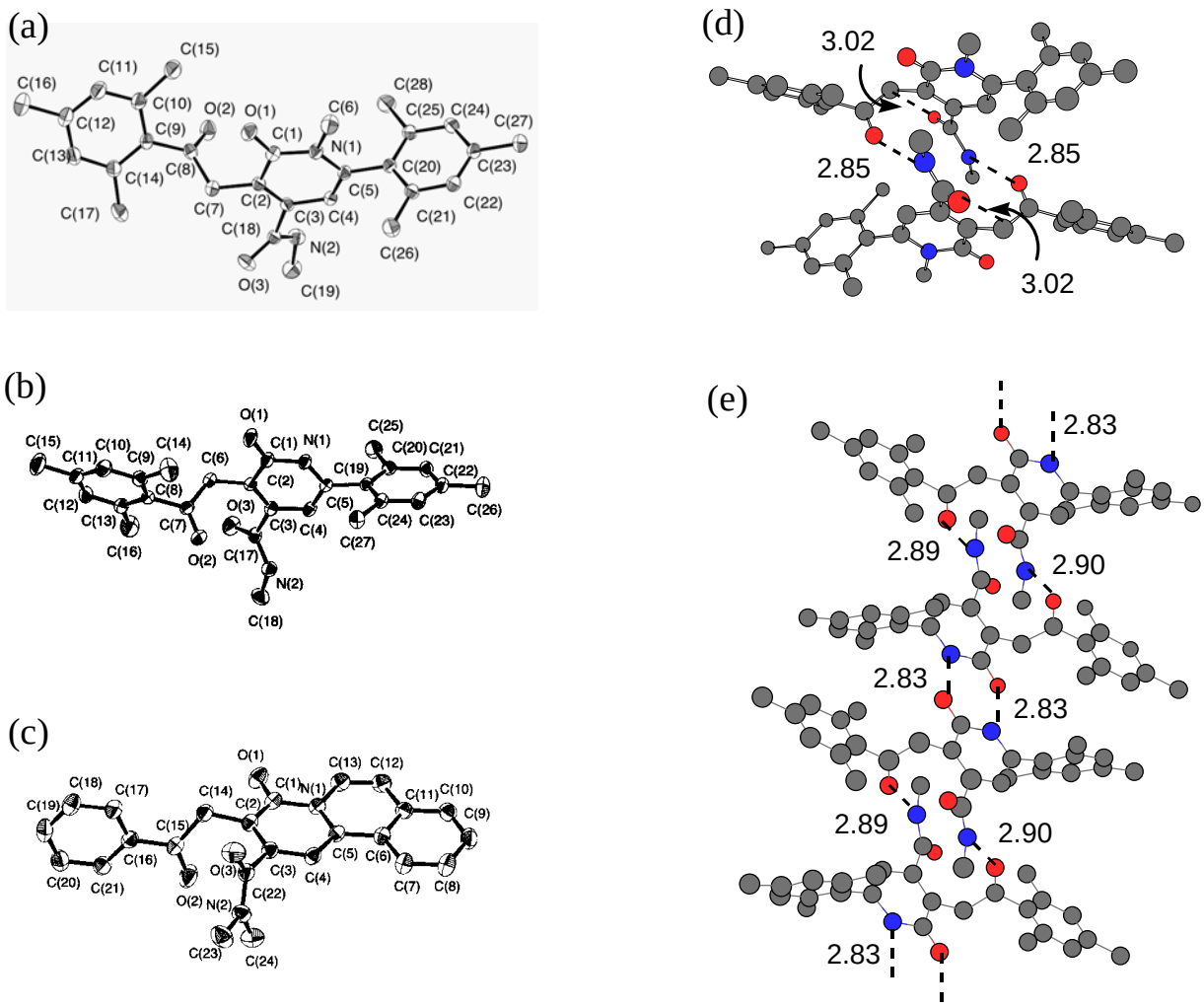



Figure 1. (a) ORTEP view of **5b**. (b) ORTEP view of **6b**. (c) ORTEP view of **8b**. (d) Hydrogen bonding in **5b**. (e) Hydrogen bonding network of **6b**.

respectively. As shown in Figure 1 (d), the compound **5b** exists in a dimeric form. A molecule of **5b** is linked to an adjacent molecule of **5b** by the N-H···O interaction between the N-H of the *N*-methyl amide group and the ketonic carbonyl oxygen (N-O distance 2.85 Å). As shown in Figure 1 (e), **6b** exists similarly in a dimeric form (N-O distances 2.89 and 2.90 Å), and each dimeric molecule arranges by the N-H···O interactions between the 2-pyridone N-H and the adjacent 2-pyridone carbonyl oxygen (N-O distance 2.83 Å), forming a one-dimensional supramolecular network. In a previous paper, we reported the inclusion ability of the one-dimensional network found in indolizino[8,7-*b*]indole derivatives.[10] Subsequently, the inclusion ability of **6b** was examined, and it was confirmed by $^1$H NMR that **6b** included $CHCl_3$ and benzene in host:guest ratios of 2:1 and 6:1, respectively.

THERMAL ANALYSIS

In mp determination, we sometimes observe sintering of the sample below the mp. Upon heating in mp apparatus, the crystals of **1b** did not melt below 300°, but there were changes in appearance. Upon heating, the crystals of **2b** melted at 185 – 187°, and bubbling occurred from the molten sample, and then the sample gradually changed to the crystals of **1a**. Upon heating, the crystals of **6b** became yellow and exclusively changed to **6a** above 300° in appearance without melting. These observations prompted us to reinvestigate the thermal properties of the keto amides (**1b** – **8b**) and the compounds (**1a** and **3a** – **8a**) with thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The TGA and DTA data were recorded at a heating rate of 10 °C/min, and are summarized in Figure 2. In the DTA of the compounds (**1b** and **2b**), two endothermic peaks (a and b) and exothermic peaks (c) are observed. The peaks (a) will be due to melting of the compounds (**1b** and **2b**), and the peaks (c) will be attributed to heat of crystallization of the product (**1a**), respectively. The peaks (b) around 290° will be due to melting of the product (**1a**), because they are almost consistent with the peak (b) in the DTA of **1a**. Similarly, the peaks (b) in the DTA of the compounds (**3b** and **6b** – **8b**) are due to melting of the products (**3a** and **6a** – **8a**), respectively, because the crystals (**3a** and **6a** – **8a**) showed the endothermic peaks at the corresponding temperatures. The DTA of the compounds (**4b** and **5b**) show only peaks (a) due to

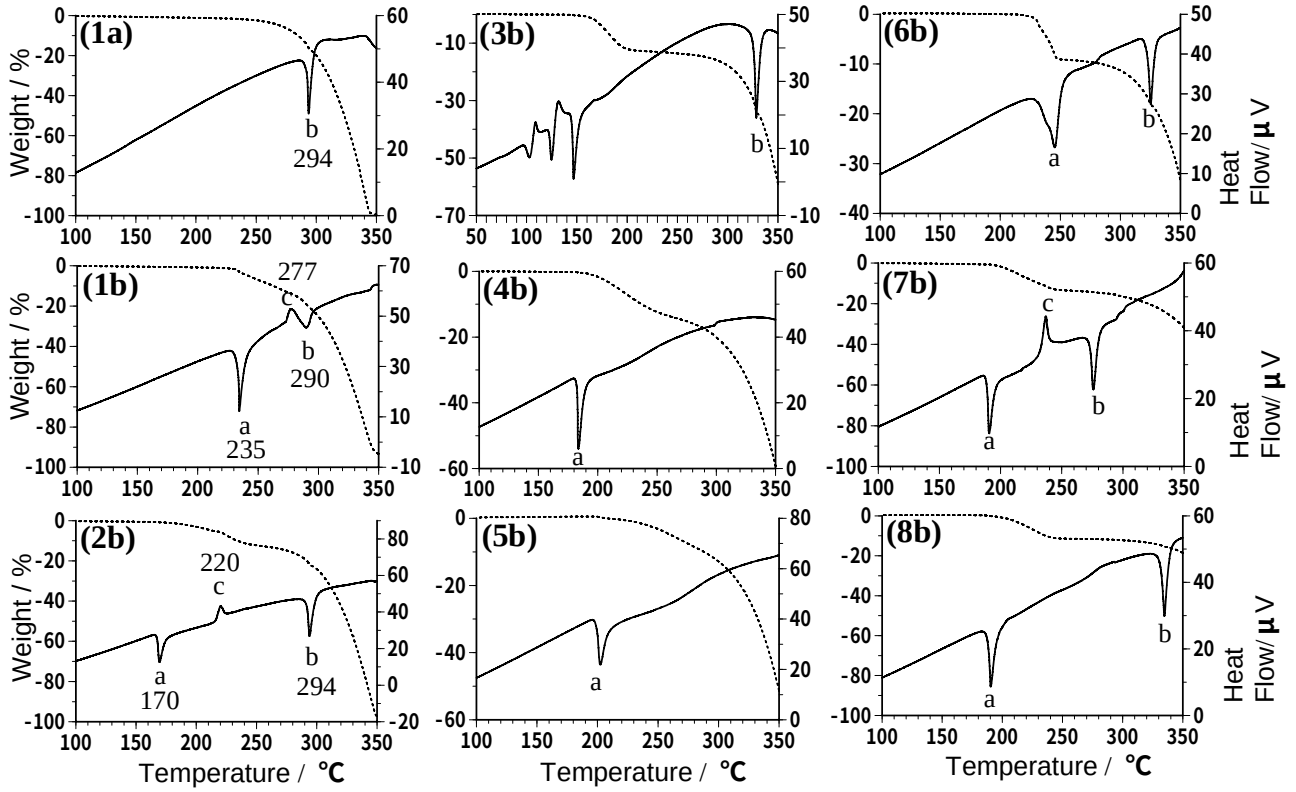



Figure 2. TGA (·····) and DTA (——) thermograms of the compounds (**1a** and **1b** – **8b**).

melting, and indicate that crystallization of the products (**4a** and **5a**) does not occur, since the temperatures of the peaks (a) were different from those of the endothermic peaks in the DTA of the crystals (**4a** and **5a**), respectively. The peaks (a) in the compounds (**6b** – **8b**) will also be due to melting, respectively. The TGA of (**1b**) and (**2b**) show that the weight losses begin at the temperatures around the peaks (a), and suggest that the structural changes from **1b** to **1a** and from **2b** to **1a** occur. Then, sublimation of the product (**1a**) is observed. The DTA thermogram of (**3b**) is complicated, and its TGA shows that the weight loss begins after three endothermic peaks are observed, suggesting the presence of several steps for the formation of **3a**. Hence, the compound (**8b**) might undergo the structural changes via (**C**) or (**D**) to give a plausible intermediate (**E**), as shown below. Elimination of $Me_2NH$ from (**E**) might afford the molten product (**8a**). Crystallization of the molten products (**1a**, **3a**, and **6a** – **8a**) during heating will be a characteristic of these compounds.

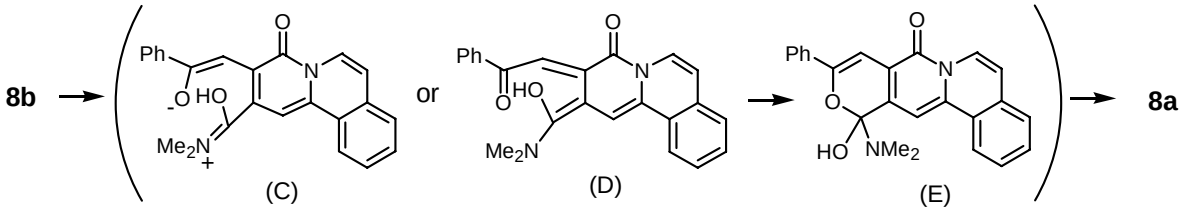



Chart 4.

Attempts to find a reversible reaction between **8b** and the supposed intermediate (**E**) were unsuccessful. The yellow crystals of **8b** became red before melting in mp apparatus, but did not show the color change by irradiation with Hg high pressure lamp or with Nd:YAG laser (355 nm).

## CONCLUSION

Aminolysis of 3,7-diarylpyrano[4,3-*c*]pyran-1,5-dione derivatives (**1a** and **3a** – **8a**) gave the keto amides (**1b** – **8b**), which upon heating returned back to the original compounds (**1a** and **3a** – **8a**) in the solid state, respectively. X-Ray crystallographic analysis of the keto amides (**5b**, **6b** and **8b**) showed the proximate orientations of the ketone and the amide groups. The TGA and DTA of the keto amides and their original compounds clarified a kind of solid-state reaction which occurred without melting in appearance, but proceeded microscopically via melting, structural change, and crystallization of the products. A compound such as **8a** would have potential usefulness as a fluorescent marker for amines, since the derived keto amides such as **(8b)** are fluorescent, and the amines are released only by heating.

## EXPERIMENTAL

All melting points are uncorrected. UV-VIS spectra were measured on a Shimadzu UV-1650PC in $CHCl_3$. $^1H$ NMR spectra were measured on a Bruker AC300 (300 MHz) in $CDCl_3$, using a $CHCl_3$

signal ($\delta_H$ = 7.26) as an internal standard. TGA and DTA thermograms were recorded on a Rigaku TG 8120. Column chromatography was performed with silica gel 60 (90 – 230 mesh, Merck) and $CHCl_3$.

**Preparation of 2b, 3b, 4b, 7b, and 8b**. A typical procedure is described for the preparation of **2b**. A mixture of **1a**[4] (80 mg, 0.20 mmol), 2M-methanolic $Me_2NH$ (1 mL, 2 mmol), and $CH_2Cl_2$ (2 mL) was stirred at rt for 1 d. The mixture was concentrated under reduced pressure to give a residue, which was crystallized from EtOAc and hexane to give **2b** (78 mg, 88%): mp 185 – 187 °C (EtOAc); UV 316 nm (ε 12100); $^1$H NMR δ = 2.28 (6H, s), 2.29 (6H, s), 2.30 (3H, s), 2.33 (3H, s), 3.05 (3H, s), 3.14 (3H, s), 4.11 (2H, br s), 6.10 (1H, s), 6.87 (2H, s), and 6.94 (2H, s). *Anal*. Calcd for $C_{28}H_{31}NO_4$: C,75.48; H, 7.01; N, 3.14. Found: C, 75.31; H, 6.95; N, 3.14. **3b** (yield 68%): mp 145 – 148 °C (MeOH); UV 340 nm (ε 18200); $^1$H NMR δ = 3.03 (3H, s), 3.06 (3H, s), 6.59 (1H, s), 7.45 – 7.90 (8H, m), and 8.03 (2H, d, *J* = 7.3 Hz). *Anal*. Calcd for $C_{22}H_{19}NO_4$: C, 73.11; H, 5.30; N, 3.88. Found: C, 72.95; H, 5.24, N, 4.13. **4b** (81%): mp 188 – 190 °C (MeOH); UV 323 nm (ε 12400); $^1$H NMR δ = 3.01 (3H, s), 3.04 (3H, s), 3.40 (3H, s), 6.06 (1H, s), 7.33 – 7.65 (8H, m), and 8.08 (2H, d, *J* = 7.2 Hz). *Anal*. Calcd for $C_{23}H_{22}N_2O_3$: C, 73.78; H, 5.92; N, 7.48. Found: C, 73.56; H, 5.89; N, 7.51. **7b** (85%): mp 196 – 197 °C (EtOAc - hexane); UV 351 nm (ε 16700); $^1$H NMR δ = 3.00 – 3.10 (4H, m), 3.04 (3H, s), 3.05 (3H, s), 6.61 (1H, s), 7.20 – 7.80 (7H, m), and 8.08 (2H, d, *J* = 7.3 Hz). *Ana*l. Calcd for $C_{24}H_{22}N_2O_3$: C, 74.59; H, 5.74; N, 7.25. Found: C, 74.19; H, 5.80, N, 7.57. **8b** (67%): mp 195 – 198 °C (EtOAc); UV-VIS 397 (ε 18000) and 419 nm (17900); Fluorescence $\lambda_{max}$ 445 and 459 nm; $^1$H NMR δ = 3.02 (3H, s), 3.08 (3H, s), 7.09 (1H, d, *J* = 7.8 Hz), 7.24 – 7.67 (7H, m), 8.09 (2H, d, *J* = 7.8 Hz), 8.27 (1H, d, *J* = 7.8 Hz), and 8.80 (1H, d, *J* = 7.8 Hz). *Anal*. Calcd for $C_{24}H_{20}N_2O_3$: C, 74.98; H, 5.24; N, 7.29. Found: C, 74.95; H, 5.20; N, 7.23.

**Preparation of 5b and 6b.** A typical procedure is described for the preparation of **5b**. A mixture of **5a**[4] (42 mg, 0.10 mmol), 40% methanolic $MeNH_2$ (0.1 mL, 1 mmol), and $CH_2Cl_2$ (0.5 mL) was allowed to stand at rt for 5 h. The mixture was concentrated under reduced pressure to give a residue, which was separated with column chromatography to give **5b** (38 mg, 84%): mp 209 – 210 °C (EtOAc – hexane); UV 324 nm (ε 11100); $^1$H NMR δ = 2.09 (6H, s), 2.30 (3H, s), 2.33 (3H, s), 2.37 (6H, s), 2.91 (3H, d, *J* = 4.8 Hz), 3.22 (3H, s), 4.21 (2H, s), 6.15 (1H, s), 6.67 (1H, q, *J* = 4.8 Hz), 6.88 (2H, s), and 6.95 (2H, s). *Anal.* Calcd for $C_{28}H_{32}N_2O_3$: C, 75.65; H, 7.26; N, 6.30. Found: C, 75.51; H, 7.33; N, 6.26. **6b** (100 %): mp > 300 °C ($CHCl_3$ – hexane); UV 323 nm (ε 9700); $^1$H NMR δ = 2.16 (6H, s), 2.20 (6H, s), 2.27 (3H, s), 2.31 (3H, s), 2.92 (3H, d, *J* = 4.9 Hz), 4.06 (2H, s), 6.16 (1H, s), 6.69 (1H, q, *J* = 4.9 Hz), 6.85 (2H, s), 6.89 (2H, s), and 10.69 (1H, br s). *Anal*. Calcd for $C_{27}H_{30}N_2O_3$: C, 75.32; H, 7.02; N, 6.51. Found: C, 75.21; H, 7.09; N, 6.53.

**Inclusion Property of 6b**. Recrystallization of **6b** from $CHCl_3$ gave an inclusion complex of **6b**·$CHCl_3$ (2:1), and that from benzene yielded **6b**·benzene (6:1). The host:guest ratios were determined by $^1H$ NMR after drying the obtained crystals at rt for 2 d. No inclusion complex was obtained by recrystallization from toluene, EtOAc, acetone, *i*-PrOH, and EtOH, respectively.

**Preparation of 6a**. A mixture of **1a** (801 mg, 2.0 mmol), 7M methanolic $NH_3$ (12 mL, 84 mmol), and $CH_2Cl_2$ (24 mL) was stirred at rt for 2 d, and concentrated under reduced pressure. To a mixture of the residue and $CH_2Cl_2$ (14 mL) was added $POCl_3$ (1.4 mL, 15 mmol). The mixture was stirred at rt for 1 d, neutralized with aq. $NaHCO_3$, and extracted with $CHCl_3$. The extracts were washed with saturated aq. NaCl, dried over $Na_2SO_4$, and concentrated under reduced pressure. Crystallization of the residue from $CHCl_3$ and MeOH gave **1a** (604 mg). The mother liquor was concentrated under reduced pressure and separated with column chromatography to give **6a** (21 mg, 2.6%. 14% based on recovered **1a**) along with **1a** (42 mg, total recovery 646 mg, 81%). **6a**: mp > 300 °C ($CHCl_3$ – MeOH); UV-VIS 282 (ε 16100) and 383 nm (17300); Fluorescence $\lambda_{max}$ 453 nm; $^1H$ NMR δ = 2.20 (6H, s), 2.28 (6H, s), 2.32 (3H, s), 2.33 (3H, s), 6.79 (1H, s), 6.88 (1H, s), 6.96 (4H, s), and 9.39 (1H, br s). *Anal*. Calcd for $C_{26}H_{25}NO_3$: C, 78.17; H, 6.31; N, 3.51. Found: C, 78.10; H, 6.16; N, 3.51.

**Preparation of 7a.** A mixture of **7c** (76 mg, 0.20 mmol), $AlCl_3$ (0.60 g, 4.5 mmol), and chlorobenzene (10 mL) was heated under reflux for 2 h. To the reaction mixture was added water, and then $CHCl_3$. The organic layer was washed (2% HCl, water, and saturated aq. NaCl), dried ($Na_2SO_4$), and concentrated under reduced pressure. Crystallization of the residue from $CHCl_3$ and hexane gave **7a** (53 mg, 78%): mp 285 – 286 °C; UV-VIS 328 (ε 11400), 421 (27300) and 447 nm (26400); Fluorescence $\lambda_{max}$ 461 nm; $^1H$ NMR δ = 3.06 (2H, t, *J* = 6.3 Hz), 4.39 (2H, t, *J* = 6.3 Hz), 7.28 – 7.52 (7H, m), 7.52 (1H, s), and 7.85 – 7.97 (3H, m). High resolution MS Calcd for $C_{22}H_{15}NO_3$: M, 341.1052. Found; 341.1048.

**Preparation of 7c.** A mixture of **3a** (316 mg, 1.0 mmol), 2-aminoethanol (0.3 mL, 4.8 mmol), and $CH_2Cl_2$ (20 mL) was stirred at rt for 1d. To the mixture was added $POCl_3$ (1.0 mL, 11 mmol). The resulting mixture was stirred at rt for 2 d, neutralized with saturated aq. $NaHCO_3$, and extracted with $CHCl_3$. The extracts were dried over $Na_2SO_4$, and concentrated under reduced pressure. Crystallization of the residue from $CHCl_3$ and MeOH gave **7c** (248 mg, 66%), which was identical with that reported in a previous paper.[4]

**Preparation of 8a**. A mixture of **3a** (316 mg, 1.0 mmol), aminoacetaldehyde dimethyl acetal (4.0 mL, 37 mmol), and $CH_2Cl_2$ (40 mL) was stirred at rt for 5 d, washed with 5% HCl to remove excess amine, dried over $Na_2SO_4$ and concentrated under reduced pressure. To the mixture of the residue and $CH_2Cl_2$ (8 mL) was added TFA (0.4 mL, 5 mmol). The mixture was stirred at rt for 1 h, washed (aq. $NaHCO_3$, and then saturated aq. NaCl), dried ($Na_2SO_4$), and concentrated under reduced pressure to give

**8c**, which was used to next Friedel-Crafts type cyclization without further purification. A mixture of the obtained **8c**, $AlCl_3$ (400 mg, 3.0 mmol), and $CH_2Cl_2$ (8 mL) was stirred at rt for 1 h, and worked up as described above to give a residue, which was triturated in MeOH to yield a powder of **8a** (219 mg, 65%): mp >300 °C; UV-VIS 287 (ε 23700), 465 (19800), and 497 nm (21300); Fluorescence $\lambda_{max}$ 506 and 537 nm; $^1$H NMR δ = 7.19 (1H, d, *J* = 8.0 Hz), 7.40 – 7.70 (6H, m), 7.62 (1H, s), 7.96 (2H, dd, *J* = 8.1 and 1.7 Hz), 8.13 (1H, s), 8.47 (1H, m), and 8.84 (1H, d, *J* = 7.8 Hz). High resolution MS Calcd for $C_{22}H_{13}NO_3$: M, 339.0896. Found: 339.0894.

**Preparation of 9a**. A mixture of **9b**[4] (103 mg, 0.30 mmol), allylamine (0.5 mL, 7 mmol), and $CH_2Cl_2$ (2 mL) was stirred at rt overnight, and concentrated under reduced pressure. To a solution of the residue in $CH_2Cl_2$ (2 mL) was added $POCl_3$ (0.5 mL, 5 mmol). The mixture was stirred at rt overnight, worked up as described above, and separated with column chromatography to give **9a** (32 mg, 28%): mp 143 – 146 °C (MeOH); UV-VIS 295 (ε 14700) and 394 nm (19900); $^1$H NMR δ = 2.19 (3H, s), 2.55 (3H, s), 4.16 (1H, dd, *J* = 14.7 and 5.5 Hz), 4.76 (1H, dd, *J* = 14.7 and 5.7 Hz), 4.83 (1H, d, *J* = 17.2 Hz), 5.13 (1H, d, *J* = 10.3 Hz), 5.77 (1H, m), 6.79 (1H, s), 7.18 – 7.45 (7H, m), 7.20 (1H, s), and 7.57 (1H, d, *J* = 8.0 Hz). *Anal.* Calcd for $C_{25}H_{21}NO_3$: C, 78.31; H, 5.52; N, 3.65. Found: C, 78.10; H, 5.57; N, 3.78.

**Preparation of 9c.** A mixture of **9b** (206 mg, 0.60 mmol), 6% methanolic $NH_3$ (1 mL, 2.8 mmol), and $CH_2Cl_2$ (3 mL) was stirred at rt overnight, and concentrated under reduced pressure. To a solution of the residue in $CH_2Cl_2$ (3 mL) was added $POCl_3$ (0.5 mL, 5 mmol). The mixture was stirred at rt overnight, worked up as described above, and separated with column chromatography to give **9c** (74 mg, 36%. 60% based on recovered **9b**) along with **9b** (82 mg, 40% recovery). **9c**: mp 257 – 258 °C ($CHCl_3$ – hexane); UV-VIS 298 (ε 15300) and 395 nm (21100); $^1$H NMR δ = 2.43 (3H, s), 2.54 (3H, s), 6.92 (1H, s), 7.10 (1H, s), 7.24 – 7.43 (7H, m), 7.57 (1H, m), and 9.66 (1H, br s). *Anal*. Calcd for $C_{22}H_{17}NO_3$: C, 76.95; H, 4.99; N, 4.08. Found: C, 77.06; H, 5.10; N, 4.05.

**Preparation of 10**. A mixture of **9c** (68 mg, 0.20 mmol), allyl bromide (0.5 mL, 6 mmol), silver (I) oxide (0.2 g, 0.9 mmol), and acetone (10 mL) was stirred at rt overnight. The mixture was separated with column chromatography and crystallized from MeOH to give **10** (54 mg, 74%): mp 93 – 95 °C (MeOH); UV-VIS 302 (ε 21100) and 368 nm (17600); $^1$H NMR δ = 2.50 (3H, s), 2.53 (3H, s), 5.03 (2H, m), 5.30 (1H, dd, *J* = 10.4 and 1.3 Hz), 5.44 (1H, dd, *J* = 17.2 and 1.6 Hz), 6.14. (1H, m), 6.98 (1H, s), 7.27 – 7.40 (6H, m), 7.50 – 7.57 (2H, m), and 7.82 (1H, s). *Anal*. Calcd for $C_{25}H_{21}NO_3$: C, 78.31; H, 5.52; N, 3.65. Found: C, 77.96; H, 5.51; N, 3.75.

**Thermal reaction of 10.** Crystals of **10** (5 mg) were sealed in a glass tube, and heated in a salt bath at 270 °C for 1 h. The $^1$H NMR spectrum of the obtained sample was almost identical with that of **9a**.

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8 A single crystal of **5b** was formed by recrystallization from EtOAc – hexane. $C_{28}H_{32}N_2O_3$, M = 444.57, triclinic, space group *P*1, *a* = 11.37(3) Å, *b* = 11.44(3) Å, *c* = 11.86(4) Å, $\alpha$ = 61.5(4)°, $\beta$ = 75.5(5)°, $\gamma$ = 65.0(4)°, *V* = 1227(4) Å$^3$, Z = 2, *R* = 0.0583, *wR* = 0.0982, GOF = 1.000. A single crystal of **6b** was formed by recrystallization from EtOAc . $C_{27}H_{30}N_2O_3$, M = 430.55, triclinic, space group *P*1, *a* = 11.236(5) Å, *b* = 11.538(5) Å, *c* = 12.213(3) Å, $\alpha$ = 61.717(18)°, $\beta$ = 61.958(20)°, $\gamma$ = 83.57(3)°, *V* = 1218.0(8) Å$^3$, Z = 2, *R* = 0.0616, *wR* = 0.1946, GOF = 1.004. A single crystal of **8b** was formed by recrystallization from EtOAc. $C_{24}H_{20}N_2O_3$, M = 384.43, triclinic, space group *P*1, *a* = 9.965(16) Å, *b* = 10.48(4) Å, *c* = 10.570(16) Å, $\alpha$ = 99.22(7)°, $\beta$ = 117.03(8)°, $\gamma$ = 92.93(6)° , *V* = 961(4) Å$^3$, Z = 2, *R* = 0.0696, *wR* = 0.2123, GOF = 1.002. Crystal data of **5b**, **6b**, and **8b** have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-648602 for **5b**, CCDC-648603 for **6b**, and CCDC-648604 for **8b**. Copies of the data can be obtained free of charge via http//www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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