Reaction of 3a, 5, 6a-Tripheny1-3, 3a-dihydro-2H-furo[3,2-b]-pyrrole-2,6 (6aH)-dione with Hydrazine, Phenylhydrazine, and Benzoylhydrazine

Mataka, Shuntaro
Department of Molecular Science and Technology, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

Suzuki, Hiroshi
Department of Molecular Science and Technology, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

Uehara, Kazuko
Department of Molecular Science and Technology, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University : Seinan Women's High School

Tashiro, Masashi
Department of Molecular Science and Technology, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

https://doi.org/10.15017/17278

出版情報：九州大学大学院総合理工学報告. 14 (3), pp.323-327, 1992-12-01. 九州大学大学院総合理工学研究科
バージョン：
権利関係：

九州大学大学院総合理工学研究科報告
第14巻 第3号 323-327頁 平成4年12月

Engineering Sciences Reports, Kyushu University
(KYUSHU DAIGAKU SOGORIKOGAKU KENKYUKA HOKOKU)
Vol. 14, No. 3, pp. 323 - 327, DEC. 1992

Reaction of 3a, 5, 6a-Triphenyl-3, 3a-dihydro-2H-furo[3,2-b]-pyrrole-2, 6 (6aH)-dione with Hydrazine, Phenylhydrazine, and Benzoylhydrazine

Shuntaro MATAKA*, Hiroshi SUZUKI*, Kazuko UEHARA**,
and Masashi TASHIRO*

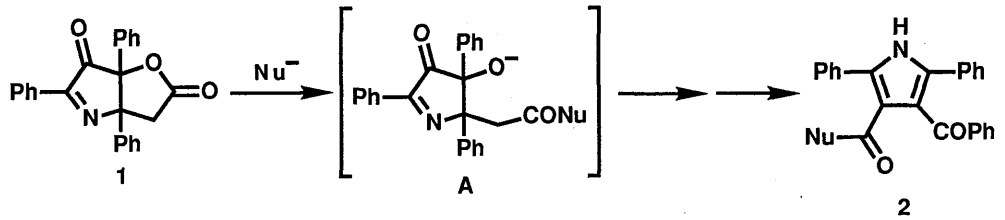
(Received August 31, 1992)

In alcoholic solution, hydrazine derivatives attack 3a,5,6a-triphenyl-3,3a-dihydro-2H-furo-[3,2-b]pyrrole-2,6(6aH)-dione **(1)** first on the lactone-ring and then the keto group. At room temperature, the reaction of **1** with hydrazine hydrate gave the hydrazino hydrazone **3a** which extruded one mole of hydrazine in refluxing ethanol, giving the hydrazone **4a**. The reaction with phenylhydrazine gave the hydrazide **5** at room temperature and the hydrazino hydrazone **3b** in refluxing ethanol. Compound **3b** could also be transformed thermally to the corresponding hydrazone **4b**. Benzoylhydrazine formed the hydrazone **4c** under more severe conditions. Compound **3b** and **4b** are solvatochromic, due to the azo-hydrazone tautomerism.

Introduction

Reactions of 3a, 5, 6a-triphenyl-3, 3a-dihydro-2H-furo[3, 2-b]pyrrole-2, 6(6aH)-dione **(1)**[1,2] with nucleophiles are of interest since **1** possesses three active sites (imino function, keto group, and lactone moiety) in the molecule. Recently, it was found that **1** undergoes a ring-transformation to polysubstituted pyrrole derivatives **2** on treatment with various amines in the presence of water (Scheme 1).[3] The above transformation is believed to be initiated by the attack of nucleophiles on the lactone-ring of **1**, followed by a cleavage of the central C(3a)-C(6a) bond of the ring-opened intermediate **A** (Scheme 1).

In the present article, the reaction of **1** with hydrazine derivatives is described.



Scheme 1

* Department of Molecular Science and Technology
** Graduate Student of Department of Molecular Science and Technology (At present; Seinan Women's High School)

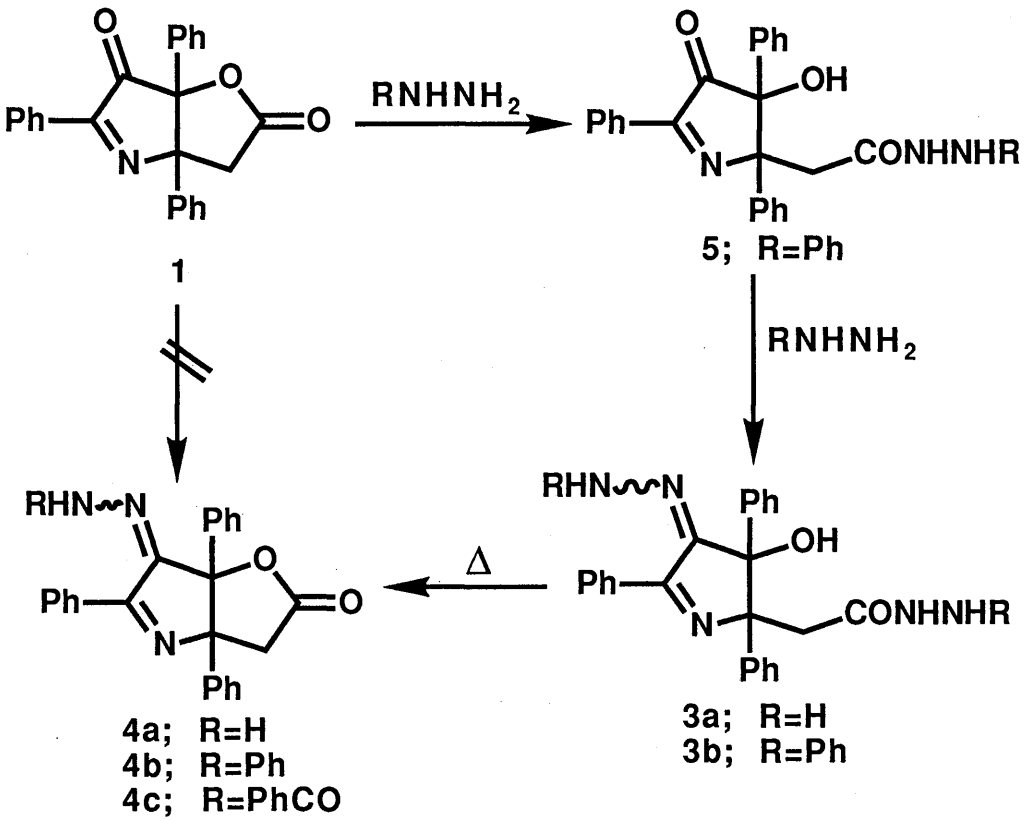
Results and Discussion

The results of the reaction of **1** with hydrazine hydrate, phenylhydrazine, and benzoylhydrazine are shown in Scheme 2.

Hydrazine reacts with both the keto group and the lactone ring of **1**. Thus, when **1** was treated with one equivalent of hydrazine hydrate in ethanol at room temperature, hydrazino hydrazone **3a** was obtained in 9% yield, together with unchanged **1** in 46% yield. The reaction of **1** with an excess of hydrazine hydrate gave **3a** in 89% yield. On the other hand, hydrazone **4a** was obtained as the major product (in 56% yield) when the reaction was carried out in refluxing ethanol, together with **3a** in 34% yield. These results indicate a thermal lactonization of **3a** into **4a**; indeed **3a** gave **4a** in 51% yield in ethanol under reflux for 24 h.

Phenylhydrazine did not attack the carbonyl function of **1** in ethanol at room temperature; it cleaved the lactone-ring, giving hydrazide **5** in 46% yield. On the other hand, the reaction in refluxing ethanol afforded hydrazino hydrazone **3b** in 26% yield. In refluxing ethanol for 24 h, **3b** produced hydrazone **4b** in 60% yield.

The reaction of **1** with the less ractive benzoylhydrazine in ethanol under reflux

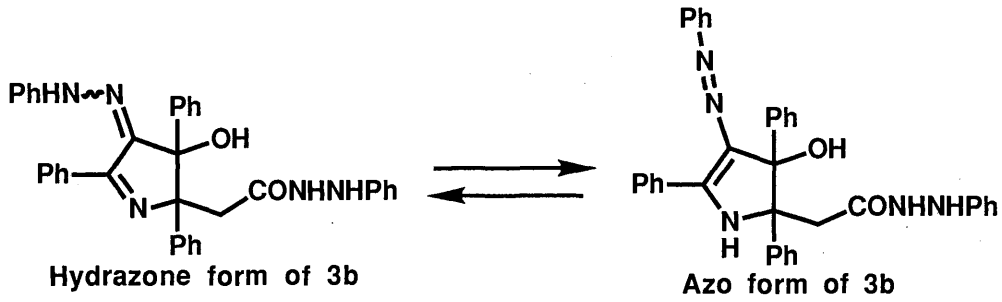


Scheme 2

afforded hydrazone **5c** in a poor yield (8%), together with a large amount of unreacted **1**. When the reaction was carried out at 130℃ using ethane-1,2-diol as a solvent, **9** was obtained in 54% yield. Neither the corresponding hydrazino hydrazone nor the hydrazide could be obtained in the above-mentioned reactions.

From these results, it may be concluded that hydrazine derivatives first attack the lactone-ring of **1** and then the keto group. The pathway for the formation of the products **3**—**5** is shown in Scheme 2.

Finally it is mentioned that **3b** is solvatochromic, due to the hydrazone-azo tautomerism[4] (Scheme 3). Pale yellow crystals of **3b** give orange-colored solutions, when dissolved in chloroform and dimethylsulfoxide. The λ max of **3b** in chloroform



Scheme 3

Table 1 Electronic Spectra of **3b** and **4b**

Compound	Solvent	λ max (nm)	log ε
3b	Chloroform	375	4.11
3b	Dimethylsulfoxide	371	4.09
4b	Chloroform	369	4.10
4b	Dimethylsulfoxide	370	4.08

showed a red-shift of 5 nm as compared with the λ max of **3b** in dimethylsulfoxide and the λ max of **4b** in both solvents (Table 1). These facts are consitent with the ^{1}H NMR spectra of **3b** and **4b**. The ^{1}H NMR spectrum of **3b** in deuteriochloroform showed that **3b** exists as a 3:1-mixture of the azo-form and the hydrazone-one in the solvent, while the latter was not detected in deuteriodimethylsulfoxide. The hydrazone-form of **4b** could not be detected in the ^{1}H NMR spectrum of **4b** in either solvent; thus **4b** takes the azo-form in both chloroform and dimethylsulfoxide.

Experimental

General. All of the melting points were determined on a Mitamurariken MELT THERMO and are uncorrected. The IR spectra were measured as KBr pellets on a Nippon Bunko IR-700. The NMR spectra were recorded at 270 MHz with a JEOL GSX-270 using TMS as an internal standard. The mass spectra were obtained on a JEOL JMS-01SG-2 mass spectrometer at 75 eV using a direct inlet system. Column chromatography was carried out on silica gel (Wako gel, C-300).

Hydrazino hydrazone 3a. A mixture of **1** (300 mg, 0.80 mmol) and hydrazine hydrate (0.1 ml, 2.0 mmol) in ethanol (10 ml) was stirred at room temperature for 2 h, giving **3a** (277 mg, 89%): Colorless prisms (ethanol); mp 173—175℃; IR 3430, 3300, 3250,

3200, and 1630 cm^{-1}; ^1H NMR (DMSO-d_6) δ =2.75 (1H, d, J=14 Hz), 3.43 (1H, d, J=14 Hz), 4.30 (2H, br s, exchanged with D_2O), 6.70−8.20 (15H, m), 7.15 (2H, br s, exchanged with D_2O), 8.42 (1H, s, exchanged with D_2O), and 9.68 (1H, br s, exchanged with D_2O); MS m/z 413 (M^+).

Found: C, 69.68; H, 5.66; N, 16.94%. Calcd for $C_{24}H_{23}N_5O_2$: C, 69.72; H, 5.66; N, 16.87%.

Phenylhydrazino phenylhydrazone 3b. A mixture of **1** (250 mg, 0.68 mmol) and phenylhydrazine (150 mg, 1.39 mmol) in ethanol (15 ml) was heated under reflux for 6.5 h; it was then cooled to room temperature. It was poured into water (40 ml) and the mixture was adjusted to pH = 6. The solid formed was filtered and chromatographed. The fraction eluted with ether gave **3b** (101 mg, 26%): Pale yellow crystalline powder (hexane-ethyl acetate); mp 212−214℃; IR 3266, 3126, 1649, and 1602 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.00 (0.75H, d, J=13 Hz), 3.46 (0.25H, d, J=14 Hz), 3.65 (0.25H, d, J=14 Hz), 3.76 (0.75H, d, J=13 Hz), 5.95 (0.75H, d, J=3.6 Hz, exchanged with D_2O), 6.51 (0.25H, s, exchanged with D_2O), 6.74−7.23 (20.5H, m), 7.53−7.64 (3.75H, m), 7.90 (0.75h, d, J= 3.6 Hz, exchanged with D_2O), 8.40 (1.5H, dd, J=8 Hz, J=1.3 Hz), 8.41−8.58 (0.5H, m), 9.29 (0.75H, s, exchanged with D_2O), and 9.40 (0.25H, s, exchanged with D_2O); ^1H NMR (DMSO-d_6) δ =3.20 (1H, d, J=14 Hz), 3.71 (1H, d, J=14 Hz), 5.76 (1H, s, exchanged with D_2O), 6.55−7.28 (20H, m), 7.73−7.79 (3H, m), 8.52−8.54 (2H, m), 8.61 (1H, s, exchanged with D_2O), 9.55 (1H, s, exchanged with D_2O), and 10.30 (1H, s, exchanged with D_2O); MS m/z 565 (M^+).

Found: C, 76.30; H, 5.59; N, 12.26%. Calcd for $C_{36}H_{31}N_5O_2$: C, 76.44; H, 5.52; N, 12.38%.

Hydrazone 4a. After a mixture of **3a** (100 mg, 0.245 mmol) in ethanol (5 ml) was heated under reflux for 24 h, it was cooled to room temperature. The solvent was evaporated and the residue was washed with ethyl acetate, giving **4a** (45 mg, 51%): Colorless prisms (ethanol); mp 215−217℃; IR 3430, 3300, 3250, and 1770 cm^{-1}; ^1H NMR (DMSO-d_6) δ =3.22 (1H, d, J=18 Hz), 3.79 (1H, d, J=18 Hz), 6.70−7.60 (13H, m), 7.26 (2H, s, exchanged with D_2O), and 8.20−8.40 (2H, m); ^{13}C NMR (DMSO-d_6) δ =42.05, 82.23, 91.43, 125.16, 126.72, 126.90, 127.48, 127.78, 128.05, 128.54, 129.22, 130.68, 132.49, 134.09, 139.43, 140.29, 167.17, and 174.49; MS m/z 381 (M^+).

Found: C, 75.43; H, 5.05; N, 11.65%. Calcd for $C_{24}H_{19}N_3O_2$: C, 75.43; H, 5.02; N, 11.02%.

Phenylhydrazone 4b. After a solution of **3b** (107 mg, 0.19 mmol) in ethanol (15 ml) was heated under reflux for 24 h, it was cooled to room temperature and then poured into water (60 ml). The precipitated solid was filtered and chromatographed. The fraction eluted with dichloromethane gave **4b** (60 mg, 68%): Pale yellow needles (hexane-ethanol); mp 214−216℃; IR 3266 and 1791 cm^{-1}; 1H NMR ($CDCl_3$) δ =3.38 (1H, d, J=19 Hz), 3.61 (1H, d, J=19 Hz), 6.79−7.22 (15H, m), 7.54−7.64 (3H, m), 8.04 (1H, s, exchanged with D_2O), and 8.42−8.47 (2H, m); ^{13}C NMR ($CDCl_3$) δ =44.49, 78.13, 83.69, 92.94, 114.63, 123.29, 126.13, 127.60, 128.36, 128.84, 129.33, 129.56, 129.72, 130.19, 130.53, 132.17, 133.10, 135.27, 140.27, 142.05, 143.31, 168.68, and 175.20; MS m/z 457 (M^+).

Found: C, 79.15; H, 5.19; N, 8.98%. Calcd for $C_{30}H_{23}N_3O_2$: C, 78.75; H, 5.07; N, 9.19%.

Benzoylhydrazone 4c. After a mixture of **1** (200 mg, 0.54 mmol) and benzoylhydrazine (164 mg, 1.20 mmol) in ethane-1,2-diol (10 ml) was heated at 130℃ for 3 h, it was cooled to room temperature. The precipitated solid was filtered and washed with water, giving **4c** (145 mg, 59%): Colorless plates (ethanol); mp 216—220℃; IR 3300, 1794, and 1707 cm^{-1}; ^1H NMR ($CDCl_3$) δ =3.47 (1H, d, J=18 Hz), 3.97 (1H, d, J=18 Hz), 7.03—7.70 (20H, m), 8.49 (2H, d, J=7 Hz), and 9.55 (1H, s, D_2O exchanged); ^{13}C NMR ($CDCl_3$) δ = 41.29, 83.02, 89.83, 125.35, 126.81, 127.01, 127.46, 127.74, 128.14, 128.35, 128.64, 128.79, 128.84, 129.45, 131.05, 131.53, 131.59, 132.63, 133.22, 138.27, 151.86, 163.25, 166.23, and 173.29; MS m/z 485 (M^+).

Found: C, 76.19; H, 4.89; N, 8.19%. Calcd for $C_{31}H_{23}N_3O_3$: C, 76.68; H, 4.78; N, 8.66%.

Phenylhydrazide 5. A mixture of **1** (250 mg, 0.68 mmol) and phenylhydrazine (760 mg, 7.2 mmol) in ethanol (15 ml) was stirred at room temperature for 5 h and poured into water (40 ml). The mixture was adjusted to pH=5 and a precipitated solid was filtered, and then chromatographed. Unidentified products were eluted off with dichloromethane and then, evaporation of the fraction eluted with ether gave **5** (160 mg, 49%): Pale yellow needles (hexane-benzene (1:1)); mp 138—140℃; IR 3328, 3028, 1748, and 1648 cm^{-1}; ^1H NMR ($CDCl_3$) δ =3.60 (1H, d, J=16 Hz), 3.80 (1H, d, J=16 Hz), 6.20—7.60 (21H, m), and 8.20 (2H, m); ^{13}C NMR (DMSO-d_6) δ = 43.74, 78.18, 83.32, 111.85, 118.38, 125.49, 126.00, 126.29, 126.49, 127.44, 127.63, 128.06, 128.30, 128.88, 130.20, 132.15, 138.87, 142.60, 147.94, 167.05, 170.32, and 200.87; MS m/z 475 (M^+).

Found: C, 75.72; H, 5.32; N, 8.56%. Calcd for $C_{30}H_{25}N_3O_3$: C, 75.77; H, 5.30; N, 8.84%.

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