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PYRIMIDINES-19

RING TRANSFORMATION OF 5-NITROURACIL INTO NITRORESORCINOLS†

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Abstract—The first intermolecular ring transformation of a uracil derivative into the benzene system is reported. Treatment of 1,3-dimethyl-5-nitrouracil (**1**) with acetone in NaOMe/MeOH afforded 6-acetonyl-5,6-dihydro-1,3-dimethyl-5-nitrouracil (**6**) which was converted into 4-nitroresorcinol (**5**) upon treatment with NaOEt/EtOH at reflux. Reaction of **1** with butanone gave two major products, 3-(5,6-dihydro-1,3-dimethyl-5-nitrouracil-6-yl)-butanone (**7**) and the 1-(uracil-6-yl)butanone isomer (**8**). Prolonged treatment of **7** with NaOEt/EtOH afforded 4-methyl-6-nitro-resorcinol (**9**) whereas **8** was converted into 2-methyl-4-nitro-resorcinol (**10**). Treatment of **1** with diethyl acetonedicarboxylate in NaOEt/EtOH afforded diethyl-2-(5,6-dihydro-1,3-dimethyl-5-nitrouracil-6-yl)-acetonedicarboxylate (**2**). Prolonged treatment of **2** with NaOEt/EtOH at reflux afforded (5,6-dihydro-1,3-dimethyl-6-nitrouracil-6-yl)-acetate (**3**). Apparently, **2** underwent a retroClaisen reaction to give **3**. Reaction of **1** with ethyl acetoacetate in NaOEt/EtOH gave adduct isomers **4** which underwent transformation reaction to give eventually 6-nitroresorcinol (**5**).

Recently, we reported conversion of 1,3-dialkyluracil derivatives into other pyrimidines[1] or into pyridines[2] by novel ring transformation reactions which involve displacement of the N_1–C_2–N_3 fragment of the 1,3-dialkyluracils by the N–C–N or C–C–N fragment of 1,3-ambident nucleophiles. We have attempted to transform 1,3-dimethyluracil into the benzene system by base-catalyzed replacement of the N_1–C_2–N_3 portion of the uracil with the C–C–C moiety of a 1,3-ambident nucleophilic agent which contains two carbon nucleophilic centers in the molecule such as diethyl acetonedicarboxylate or ethyl acetoacetate, but the corresponding 2,4-dihydroxyisophthalic acid or 2,4-dihydroxy-acetophenone could not be obtained from the reaction mixture. We found, however, that 1,3-dimethyl-5-nitrouracil (**1**), the C-6 position of which is very susceptible to nucleophilic attack, underwent ring transformation reaction to afford nitroresorcinols.

When **1** was treated with diethyl acetonedicarboxylate in NaOEt/EtOH at reflux, formation of two UV absorbing products was observed by tlc. These products could not be cleanly separated by chromatography. The PMR spectrum of the semipurified product showed it to be a 3:1 mixture of closely related isomers in which the olefinic H-6 was absent and two N-methyl and two ester ethyl groups were present. These isomers are most probably the adducts **2**, each of which bears three asymmetric centers in the molecule. Prolonged treatment of the mixture **2** with NaOEt/EtOH afforded (5,6-dihydro-1,3-dimethyl-5-nitrouracil-6-yl)acetic acid (**3**) which was isolated as a crystalline racemate in 42% yield. Obviously, **2** underwent a retro-Claisen reaction to form the uracilyl-acetate **3**.

Treatment of **1** with ethyl acetoacetate instead of diethyl acetonedicarboxylate in NaOEt/EtOH gave a mixture of addition products (**4**). The PMR spectrum of the mixture showed two acetyl signals at δ 2.12 and 2.23 with relative intensities of 1:3, and the overall spectral pattern was very similar to that of **2**. Prolonged treatment of **4** with NaOEt/EtOH at reflux resulted in the formation of a small amount of 4-nitroresorcinol (**5**) which was isolated in crystalline form in 12% yield.

A plausible mechanism for the formation of **4** to **5** would be abstraction of the most acidic α-proton of **4** by base followed by cleavage of the Nl-C6 bond to form [A]. Dissociation of a proton from the terminal methyl group of [A] and attack by the resulting carbanion on C4 would afford the ureido [B] from which 4-hydroxy-5-nitrosalicylate **5'** would form by elimination of the urea and aromatization. Compound **5** would arise from **5'** by hydrolysis of the ester followed by decarboxylation.

We also found that even acetone can form an addition product with **1** in base. The acetonyl compound **6** was isolated as a crystalline racemate in 74% yield after treatment of **1** with acetone in NaOMe/MeOH. The PMR spectrum of **6** showed three methyl signals at δ2.12 (CAc), 2.91 and 3.10(NMe) in addition to a narrow doublet at δ 5.72 for H-5, a double triplet at δ 4.35 for H-6 and a multiplet at δ 2.98 for the α-methylene signals. These data are consistent with structure **6**. Further treatment of **6** with NaOEt/EtOH at reflux afforded a mixture from which **5** was isolated in 12% yield.

When butanone was used instead of acetone in the above reaction, two major products were obtained. The structure of one of the products was established as **7** by PMR analyses which showed the presence of four methyl groups in the molecule. The methyl signal at δ 1.14 is a doublet which indicates the involvement of the C-3 position of butanone in the adduct formation. Additional signals at δ4.46 (double doublet for H-6, $J_{5,6}$ = 1.5 and $J_{6,\alpha}$ = 7.0 Hz), 5.76 (doublet for H-5, $J_{5,6}$ = 1.5 Hz) and 2.05 (apparent quintet for H-α) firmly establish that the uracil and butanone are linked between C-6 of the former and C-3 of the latter. The PMR spectrum of the other product showed three methyl signals (a triplet at δ0.92 and two NMe singlets at δ2.91

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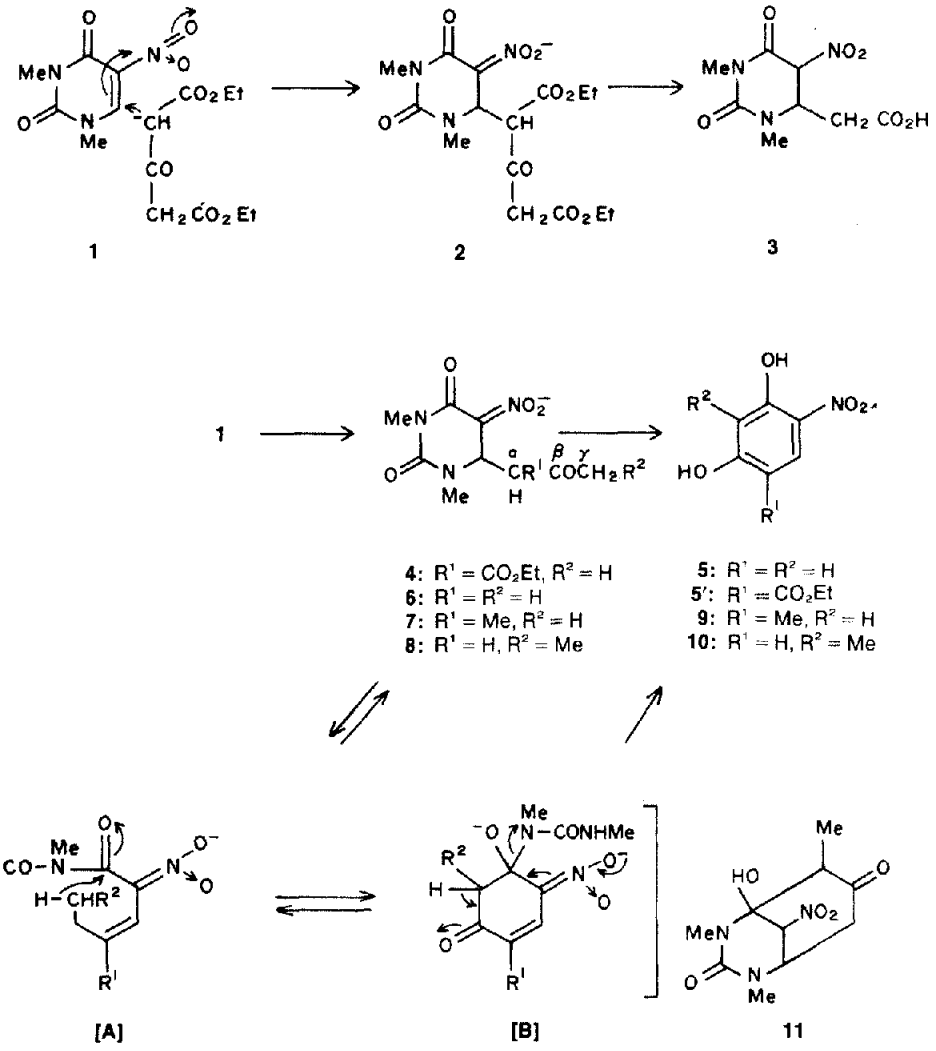

and 3.10) and two methylene signals (a quartet at δ2.46 and a doublet at δ 2.98) in addition to a doublet for H-5 (δ5.74) and a double triplet for H-6 (δ4.57). These PMR data are only consistent with structure **8**. These structures were further confirmed by their conversion into the benzene ring system. Upon treatment with NaOEt/EtOH at reflux, **7** afforded the known 4-methyl-6-nitroresorcinol (**9**)[3], whereas **8** was converted into 2-methyl-4-nitroresorcinol (**10**). The PMR spectrum of the latter, which showed two doublets at δ6.45 and 7.93 (for H-4 and H-5, respectively, $J_{4,5} = 9.4$ Hz) in addition to a methyl singlet at δ2.19 and an exchangeable signal integrated for two protons at δ11.3, established structure **10**.

When a mixture of **7** and **8** was treated with NaOEt/EtOH at reflux, occasionally a third product was formed in the reaction mixture. In one experiment, a mixture of **7** and **8** in approximately 1:1 proportion was converted into a mixture from which **9** and the third product were isolated in crystalline form but **10** could not be detected in the reaction mixture. The structural assignment of the third product to be 2,3,8-trimethyl-9-nitro-2,4-diazabicyclo-[3.3.1]nonan-3,7-dione (**11**) was made on the basis of PMR data. In this spectrum there are three methyl signals, one of which (at δ1.10) splits into a doublet, indicating the presence of a CHMe system in the molecule. Two signals at δ5.65 (narrow doublet) and at δ4.18 (narrow triplet) are assigned based on their chemical shifts to the protons attached to carbons derived from C-5 and C-6 of the uracil, respectively (namely, H-9 and H-5, respectively, of the bicyclo[3.3.1]nonane system in **11**). The shape of the H-5 signal (narrow triplet) indicates that the proton is coupled only with one of the adjacent methylene protons at C-6. The axial proton on C-6 resonates at δ2.40 as a doublet while the equatorial proton at δ2.52 resonates as a double doublet ($J_{6a,6e} = 18.0$ Hz). The dihedral angles defined by H-5 and H6a, and by H-5 and H-6e are in the range of 70–80° and 40–50°, respectively. Also, one rapidly exchangeable proton signal is shown at δ6.80. All these PMR data are fully consistent with structure **11**. Further conversion of **11** into 2-methyl-4nitroresorcinol (**10**) did not occur.

The transformation of **7** into **9** or **8** into **10** most probably proceeded by a mechanism similar to the conversion of **4** into **5**. Thus, the α-proton was abstracted by base followed by cleavage of the N1–C6 linkage giving rise to the open-chain intermediate [A] from which a

proton of the terminal methyl group dissociated and the resulting carbanion attacked on the C4 position to give rise to the ureido intermediate [B]. Simulatneous elimination of the urea and aromatization resulted in the formation of the resorcinols **9** and **10**. For the formation of **11** from **8**, apparently a proton from the γ-position rather than the one from the α-methylene was abstracted by base, and the resulting carbon nucleophile attacked C4 to form the bicyclic product **11**.

Though a number of pyrimidine to pyrimidine[1,4] and pyrimidine to pyridine[2,5-8] transformation reactions are known, examples of intermolecular pyrimidine to benzene ring transformations are rare.[9] Only recently, 5-nitropyrimidine[8] and 5-nitro-2(1H)-pyrimidinone[10] were converted into p-nitrophenol and its derivatives. Our present work, however, represents to the best of our knowledge, the first *intermolecular* transfragment conversion[12] of a uracil derivative into the benzene system.

EXPERIMENTAL

All mp values are uncorrected and were determined in open capillary tubes using a Thomas–Hoover apparatus. PMR spectra were recorded on a JEOL-PFT-100 spectrometer with TMS as an internal standard. Chemical shifts are reported in ppm (δ) and signals are described as s(singlet), d(doublet), t(triplet), m(multiplet), dd(double doublet) and dt(double triplet). Values given for coupling constants are first order. UV spectra were obtained with a Cary Model 15 recording spectrometer. Tlc was performed on 250μ silica gel plates (Analtech Inc., Newark, Delaware) and spots were visualized by UV light. Column chromatography was done using Woelm silica gel (70–230 mesh). Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

(5,6-*Dihydro*-1,3-*dimethyl*-5-*nitrouracil*-6-yl)*acetic acid* (**3**). A mixture of **1** (1.85 g, 0.01 mol) and diethyl acetonedicarboxylate (5 ml) in freshly prepared 0.67M ethanolic NaOEt (30 ml) was heated at reflux for 20 h. After cooling to room temperature, the mixture was neutralized with Dowex 50 (H^+). The resin was filtered and washed with MeOH. The combined filtrate and washings were evaporated *in vacuo* to dryness, and the residue chromatographed on a column of silica gel (30 × 3 cm) using $CHCl_3$–MeOH (30:1 v/v) as the eluent. The UV absorbing fractions were collected and concentrated to dryness to give 1.16 g of a syrup. Major peaks in PMR [$CDCl_3$: δ 1.29 (t, CH_2CH_3), 3.07 (s, NMe), 3.29 (s, NMe), 4.20 (q, CH_2CH_3), 4.54 (m, H-6), 4.90 (m, H-α), 5.30 (d, H-5) contamination of another product was shown by the presence of many other peaks, especially a doublet at δ 5.19] showed this product to be a 3:1 mixture of isomers **2**.

2(1.0 g) was dissolved in NaOEt/EtOH (prepared by dissolving 180 mg of Na in 30 ml of EtOH), and the solution refluxed for 26 h. The mixture was cooled to room temperature and neutralized with Dowex 50 (H^+). The resin was filtered and washed with MeOH. The combined filtrate and washings were concentrated to dryness *in vacuo*, and the residue crystallized from EtOH to give 249 mg (42%) of **3**, m.p. 184–185° (dec). PMR (DMSO-d_6) δ2.75 (2H, d, 2Hα, $J_{6,\alpha}$ = 6.71 Hz), 2.96 (3H, s, NMe), 3.09 (3H, s, NMe), 3.09 (3H, s, NMe), 4.55 (1H, dt, H-6, $J_{5,6}$ = 1.83, $J_{6,\alpha}$ = 6.71 Hz), 5.88 (1 H, d, H-5, $J_{5,6}$ = 1.83 Hz). UV $\lambda_{max}^{H_2O}$ 325 nm (ϵ 6500), λmin 265 (2200). Found: C, 39.50; H, 4.70; N, 16.87. Calc. for $C_8H_{11}N_3O_6$: C, 39.19; H, 4.52; N, 17.14%.

Reaction of **1** *with ethyl acetoacetate.* A mixture of **1** (1.89 g, 0.01 mol) and ethyl acetoacetate (5 ml) in NaOEt/EtOH (prepared from 460 mg of Na and 30 ml of EtOH) was heated at reflux for 20 h. After cooling to room temperature, the mixture was neutralized with Dowex 50 (H^+). The resin was filtered and washed with MeOH. The combined filtrate and washings were concentrated to dryness and the residue chromatographed over a column of silica gel (30 × 3 cm) using $CHCl_3$–MeOH (20:1 v/v) as the eluent. The UV absorbing fractions were collected and concentrated to dryness to give 1.88 g of **4** as a syrup. The major peaks in PMR ($CDCl_3$) were as follows: 1.29 (t, CH_2CH_3), 2.23 (s, $COCH_3$), 3.07 (s, NMe), 3.28 (s, NMe), 4.21 (q, CH_2CH_3), 4.75 (m, H-5), 5.21 (m, H-α), 5.31 (d, H-5).

A solution of **4** (1.5 g) in 0.75 M NaOEt/EtOH (40 ml) was refluxed for 20 hr, cooled to room temperature, neutralized with Dowex 50 (H^+), the resin filtered and the filtrate concentrated to dryness to a syrup which was chromatographed over a column of silica gel (30 × 3 cm) using hexane–EtOAc (7:3 v/v) as the eluent. The fast running yellow fractions were collected, evaporated *in vacuo*, and the residue recrystallized from water to give 4-nitroresorcinol **5** (18 mg, 11.6%), m.p. 114–116° (lit[11] m.p. 113°). UV $\lambda_{max}^{H_2O}$ 347 nm (ϵ 9800) 243 (shoulder) (4400) 216 (9100), λ_{min} 260 (1900). Found: C, 46.57; H, 3.42; N, 8.93. Calc. for $C_6H_5NO_4$: C, 46.46; H, 3.25; N, 9.03%.

6-*Acetonyl*-5,6-*dihydro*-1,3-*dimethyl*-5-*nitrouracil* (**6**). A mixture of **1** (1.85 g, 0.01 mol) and acetone (10 ml) in methanolic MeONa [prepared by dissolving metallic Na (460 mg, 0.02 mol) in 60 ml of MeOH] was heated at reflux for 2 h. After cooling to room temperature, the mixture was neutralized with Dowex 50 (H^+). The resin was filtered, washed with MeOH, and the combined filtrate and washings evaporated *in vacuo* to dryness. The residue was crystallized from MeOH to give 1.79 g (73.5%) of **2**, m.p. 139–140°. PMR (DMSO-d_6) δ2.12 (3H, s, Ac), 2.91 (3H, s, NMe), 2.98 (2H, m, CH_2), 3.10 (3H, s, NMe), 4.35 (1H, m, H-6), 5.72 (1H, d, H-5, $J_{5,6}$ = 2.8 Hz). UV $\lambda_{max}^{H_2O}$ 325 nm (ϵ 9960), λ_{min} 260 (3000). Found: C, 44.47; H, 5.59; N, 17.26. Calc. for $C_9H_{13}N_3O_5$: C, 44.45; H, 5.39; N, 17.28%.

4-*Nitroresorcinol* (**5**) *from* **6**. **6** (1.622 g, 6.6 mmol) was treated with 0.67M NaOEt/EtOH (30 ml) at reflux for 20 h. The mixture was cooled to room temperature, neutralized with Dowex 50 (H^+), filtered, and the filtrate concentrated to dryness *in vacuo*. The residue was chromatographed over a silica gel column (30 × 3 cm) using hexane–EtOAc (7:3 v/v) as the eluent to give 123 mg (12%) of 4-nitroresorcinol (**6**) identical in all respects with a sample obtained by an alternate method.

Reaction of **1** *with butanone.* A mixture of **1** (1.85 g, 0.01 mol) and butanone (10 ml) in 0.33 M NaOMe/MeOH (freshly prepared from 460 mg of Na and 60 ml of MeOH) was heated at reflux for 2 h, cooled to room temperature, and neutralized with Dowex 50 (H^+). The resin was filtered, washed with MeOH, and the combined filtrate and washings concentrated to dryness to a syrup which was chromatographed over a silica gel column (30 × 3 cm) using $CHCl_3$–MeOH (30:1 v/v) as the eluent. The UV absorbing fractions (two spots on tlc $CHCl_3$–MeOH 9:1 v/v) were collected and concentrated to dryness and crystallized from MeOH to give 698 mg (31%) of 3-(5,6-dihydro-1,3-dimethyl-5-nitrouracil-6-yl)butanone (**7**), m.p. 185–186° (dec). UV $\lambda_{max}^{H_2O}$ 327 nm (ϵ 10450), λmin 260 (3200). PMR (DMSO-d_6) δ 1.14 (3H, d, $CHCH_3$), 2.16 (3H, s, Ac), 2.97 (3H, s, NMe), 3.09 (3H, s, NMe), 3.14 (1H, quintet, H-α, $J_{6,\alpha}$ = 7.02 Hz), 4.46 (1H, dd, H-6), $J_{6,\alpha}$ = 7.02, $J_{5,6}$ = 1.53 Hz), 5.76 (1 H, d, H-5, slowly exchangeable, $J_{5,6}$ = 1.53 Hz). Found: C, 44.56; H, 5.69; N, 15.47. Calc. for $C_{10}H_{15}N_3O_5$-2/3 H_2O: C, 44.61; H, 6.11; N, 15.61%.

The mother liquor of crystallization was concentrated and the residue recrystallized from EtOH to give 635 mg (25%) of 1-(5,6-dihydro-1,3-dimethyl-5-nitrouracil-6-yl)butanone (**8**), m.p. 178–180° (dec). UV $\lambda_{max}^{H_2O}$ 326 nm (ϵ 9584), λmin 260 (2730). PMR (DMSO-d_6) δ 0.92 (3H, t, CH_2H_3), 2.46 (2H, q, CH_2CH_3), 2.91 (3H, s, NMe), 2.98 (2H, q, α-CH_2), 3.10 (3H, s, NMe), 4.57 (1H, dt, H-6, $J_{5,6}$ = 1.8, $J_{6,\alpha}$ = 6.3 Hz), 5.74 (1H, d, H-5, $J_{5,6}$ = 1.8 Hz). Found: C, 46.49; H, 5.97; N, 16.16. Calc. for $C_{10}H_{15}N_3O_5$: C, 46.69; H, 5.84; N, 16.34%.

4-*Methyl*-6-*nitroresorcinol* (**9**). A mixture of **7** (316 mg, 1.23 mmol) and NaOEt/EtOH (36 mg of Na in 20 ml of EtOH) was heated at reflux for 20 h. The mixture was cooled to room temperature, neutralized with Dowex 50 (H^+), and the resin removed by filtration. The filtrate was concentrated *in vacuo* and the residue dissolved in $CHCl_3$ (5 ml). Silica gel (5 g) was added to the solution and the mixture concentrated *in vacuo*. The residue was placed on a column of silica gel (30 × 3 cm) and the column was washed with a mixture of hexane and EtOAc (7:3 v/v). Appropriate fractions were collected and concentrated

to dryness and the residue recrystallized from C_6H_{14}–$CHCl_3$ to afford 56 mg (27%) of **9**, m.p. 121–123° (lit.[3] 125°). UV $\lambda_{max}^{H_2O}$ 361 nm (ϵ8240), 245 (shoulder, 4300), 214 (9460), λ_{min} 265 (1400). PMR ($CDCl_3$) δ 2.21 (3H, s, CH_3), 6.46 (1H, s, H-5), 7.89 (1H, s, H-2), 10.84 (2H, s, OH). Found: C, 49.88; H, 4.38; N, 8.25. Calc. for $C_7H_7NO_4$: C, 49.71; H, 4.17; N, 8.28%.

2-*Methyl-4-nitroresorcinol* (**10**). The preparation of **10** from **8** followed the same procedure as described for **9** from **7**. The yield of **10** was 13%, m.p. 124–125°, UV $\lambda_{max}^{H_2O}$ 351 nm (ϵ 11900), 241 (shoulder, 4370), λ_{min} 266 (5630). PMR ($CDCl_3$) δ 2.19 (3H, s, CH_3), 6.45 (1H, d, H-4, $J_{4,5}$ = 9.5 Hz). 7.93 (1H, d, H-5, $J_{4,5}$ = 9.5 Hz), 11.32 (2H, s, OH). Found: C, 49.88; H, 4.34; N, 8.05. Calc. for $C_7H_7NO_4$: C, 49.71; H, 4.17; N, 8.28%.

2,3,8-*Trimethyl-9-nitro-2,4-diazabicyclo*[3.3.1]*nonan-3,7-dione* (**11**). A crude condensation product (1.54 g, containing **7** and **8** in a 1:1 proportion according to PMR) of **1** and butanone was dissolved in NaOEt/EtOH (prepared by dissolving 416 mg of Na in 40 ml of EtOH), and the mixture heated at reflux for 20 h. The mixture was cooled to room temperature, neutralized with Dowex 50 (H^+), and the resin filtered and washed with EtOH. The combined filtrate and washings were concentrated to dryness. The residue was triturated with a small amount of $CHCl_3$. The insoluble crystals were collected by filtration and recrystallized from EtOH to give 290 mg (29%) of **11**, m.p. 166–167°, UV $\lambda_{max}^{H_2O}$ 297 nm (ϵ 4700), λ_{min} 256 (2500). PMR (DMSO-d_6) δ 1.10 (3H, d, $CHCH_3$), 2.40 (1H, d, H-6a, $J_{6a,6e}$ = 18.0, $J_{5,6a}$ = 0 Hz), 2.52 (1H, dd, H-6e, $J_{6a,6e}$ = 18.0, $J_{5,6}$ = 1.8 Hz), 2–2.5 (1H, m, H-8), 4.18 (1H, t, H-5, $J_{5,6e} \cong J_{5,6} \cong$ 1.8 Hz), 5.65 (1H, d, H-9, $J_{5,9} \cong$ 1.8 Hz), 6.80 (1H, s, 1-OH). Found: C, 46.65; H, 6.03; N, 16.30. Calc for $C_{10}H_{15}N_3O_5$: C, 46.69; H, 5.88; N, 16.33%.

The $CHCl_3$ filtrate was placed on a column of silica gel (30 × 3 cm) and the column was washed with C_6H_{14}–EtOAc (7:3 v/v). Compound **9** was eluted from the column. After recrystallization, 353 mg (23%) of **9** was obtained, m.p. 121–123°. IR and PMR spectra of this sample were identical with those of **9** prepared from pure **7**.

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