Transformation of a Spirobarbituric Acid *via* Aminobarbituric Acid-Hydantoin Rearrangement

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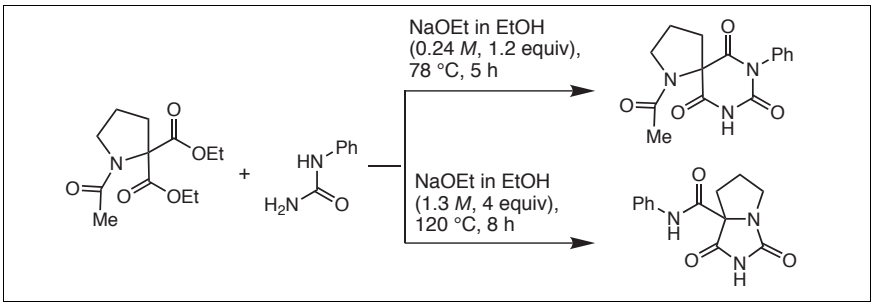

A successful application of the aminobarbituric acid-hydantoin rearrangement to produce a bicyclic carbamoylhydantoin from an intermediate spirobarbituric acid is reported. 7a-Phenylcarbamoyl-tetrahydro-1*H*-pyrrolo[1,2-*c*]imidazole-1,3(2*H*)-dione (**8**) was obtained in a one-pot multistep reaction of 1-acetyl-2,2-bis(ethoxycarbonyl)pyrrolidine (**5**) and phenylurea in the presence of sodium ethoxide. Under less severe conditions, **5** and phenylurea were reacted to afford 1-acetyl-7-phenyl-triaza[4,5]decane-6,8,10-trione (**6**). The structural elucidation of the bicyclic hydantoin **8** and the spirobarbituric acid **6** was based on relevant nmr signals in accordance with those of reference compounds, *i.e.* monocyclic hydantoins **4a**,**b** and acetamidobarbituric acids **2a**-**c**. The latter compounds were newly prepared from diethyl acetamidomalonates **1** and phenylurea.

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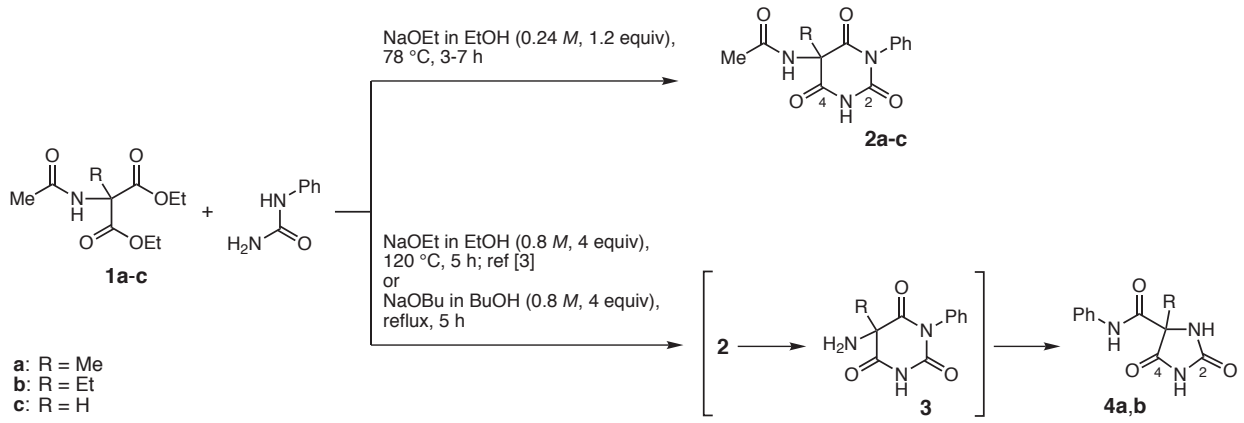
Hydantoins have been the subject of considerable interest in drug discovery because of their wide range of biological activities. With four possible points of diversity, this heterocyclic structure represents a significant molecular scaffold in combinatorial chemistry; see [1] for a review and [2] for some recent publications on hydantoin chemistry. In a previous report, we have described the aminobarbituric acid-hydantoin rearrangement as an attractive synthetic entry to tri- and tetra-substituted 5-carbamoylhydantoins [3]. 1,5-Disubstituted barbituric acids with an additional amino group at position 5 undergo a base-catalyzed ring contraction to afford 5-carbamoylhydantoins in which the substituent at the carbamoyl moiety originates from the 1-substituent at the nitrogen of the parent barbituric acid. A special case of the rearrangement comprises the conversion of barbituric acids with an unsubstituted 5-amino group (*e.g.* **3**) to 5,5-disubstituted hydantoins with two unsubstituted ring nitrogens (*e.g.* **4**, Scheme 1). Barbituric acids with a 5-NH_2 substituent (*e.g.* **3**) could either be prepared by a route *via* corresponding 5-azido derivatives [4,5], or formed as intermediates of the one-pot synthesis using substituted diethyl acetamidomalonates (**1**) and ureas as starting materials [4]. The latter transformation includes the cyclocondensation to 5-acetamidobarbituric acids (*e.g.* **2**), deacetylation, deprotonation at the ring nitrogen, ring opening and recyclization due to the nucleophilic attack of the amino group at the intermediate isocyanate [3,4]. Compared to alkyl ureas, the reaction of aryl ureas with **1** gives rise to the rearrangement to hydantoins under less rigorous conditions [3,4]. Therefore, the synthesis of 1-phenyl acetamidobarbituric acids **2** is not so straightforward. In order to prepare both **2**, as well as 4-phenylcarbamoyl hydantoins **4**, we have studied the reaction of three diethyl acetamidomalonates (**1a**-**c**) with phenylurea. Moreover, the application of these reactions to the pyrrolidine substrate **5** (Scheme 2) was investigated.

The synthesis of the 5-ethyl hydantoin **4b** (Scheme 1) was carried out according to the described method [4] in the presence of sodium ethoxide in ethanol in a sealed tube at 120 °C. Next it was examined whether ethanol could be replaced by higher-boiling 1-butanol and thus sodium ethoxide by butoxide to allow for a reaction process in an open vessel. This was indeed the case, and **4a** was obtained from **1a** by this method. Both **4a** and **4b** were then used as reference compounds to investigate the reactions of phenylurea with alkylated diethyl acetamidomalonates **1a** and **1b** under less severe conditions. Product mixtures were obtained which contained the corresponding hydantoins **4a** and **4b**, respectively, besides the desired acetamidobarbituric acids **2a** and **2b**, respectively, and the latter compounds could be isolated. The purification of **2a** and **2b** was achieved by single recrystallizations from ethanol. The new 2-acetamido-1-

Scheme 1



phenylbarbituric acid (**2c**) was similarly prepared from **1c** and phenylurea. However, our attempts to synthesize a corresponding hydantoin with a 5-phenylcarbamoyl rest as the only substituent failed.

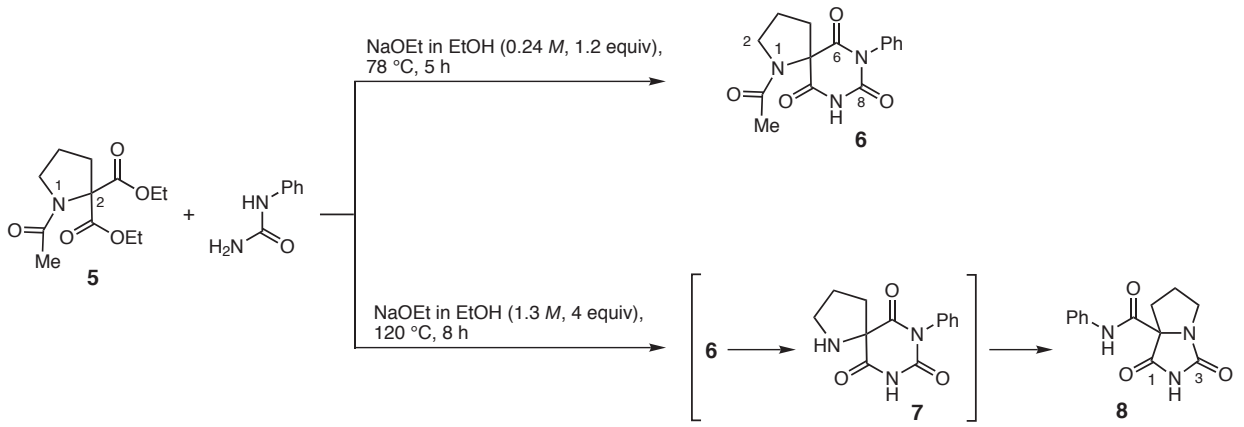
The proline-derived diester **5** [6,7] (Scheme 2) was prepared from **1c** (Scheme 1) and 1,3-dibromopropane with benzyltriethylammonium chloride as phase transfer catalyst [7]. The utilization of **5** as the substrate of the aforementioned conversions let us anticipate interesting products. Actually, the spirobarbituric acid **6** was obtained from **5** and phenylurea (Scheme 2). Some other spirobarbituric acids with a dihydropyrrole [8] or a pyrrolidinone unit [9] are known. In N(1), N(3)-unsubstituted barbituric acids, the spiro-connected pyrrolidinone moiety was recently designed as a constrained linker structure to facilitate inhibition of matrix metalloproteinases [10].

8, can be envisaged as a result of an undesired decarbamoylation of **8**, either through direct attack of the nucleophile ethoxide or through the repulsion of phenyl isocyanate *via* an E1cB mechanism and subsequent reaction with ethoxide.

The formation of **8** involves ring closure and deacetylation of the 'protected' aminobarbituric acid **6**. The key step to **8** is the ring-opening/recyclization of the intermediate spiro compound **7**, thus the transformation of the spiro-connected five-membered cycle to an anellated ring.

Several features in the nmr spectra for **6** and **8** allowed for their structural elucidation and were in accordance with the monocyclic analogues **2** and **4**, respectively. In the ^{13}C nmr spectra of barbituric acids **2** and **6** the first carbonyl resonance appeared at 149-152 ppm (urea CO),

Scheme 2



When **5** and phenylurea were reacted under more rigorous conditions the bicyclic hydantoin **8** was directly attained. The product **8** was accompanied by ethyl *N*-phenylcarbamate. Its formation, and thus the low yield of

and the ^{13}C nmr shifts of the other three carbonyl carbons occurred close together at 167-171 ppm. In contrast, the ^{13}C nmr spectra of carbamoyl hydantoins **4** and **8** showed three distinct carbonyl signals at 156-161 ppm (urea CO),

164-166 ppm (carbamoyl CO), and 171-174 ppm. Expectedly, the nmr shifts of the phenyl protons depended on its position either at an imide (in **2** and **6**) or amide nitrogen (in **4** and **8**). In the latter case, the signals appeared apart from each other at 7.1-7.2 ppm (H-4'), 7.3 ppm (H-3'), and 7.6-7.7 ppm (H-2'). The ^{13}C nmr spectra of **2** and **6** exhibited signals for the phenyl carbons at 129 ppm (C-4'), 129-130 ppm (C-2', C-3'), and 135 ppm (C-1'). The pattern of the corresponding ^{13}C nmr signals in the case of **4** and **8** was clearly different with four distinct signals at 121 ppm (C-2'), 124 ppm (C-4'), 129 ppm (C-3'), and 138 ppm (C-3).

In summary, we have examined the ethoxide-promoted formation of **8** from **5** and phenylurea in the course of a one-pot multistep reaction. This is the first example of the aminobarbituric acid-hydantoin rearrangement in which a cyclic secondary amine (in structure **7**) served as the nucleophile for the intramolecular trapping of a postulated intermediate isocyanate. As a consequence, the nitrogen of the attacking amino group becomes the bridgehead nitrogen of the newly formed anellated hydantoin (structure **8**). Bicyclic hydantoins have attracted much attention in medicinal chemistry and organic synthesis particularly in the preparation of hydantoin-containing polycyclic scaffolds using solid-phase methods [1,11]. Several derivatives of the tetrahydro-1*H*-pyrrolo[1,2-*c*]imidazole-1,3(2*H*)-dione system have been described. Compound **8**, however, is the first example of a 7a-carbamoyl-substituted derivative of that system.

EXPERIMENTAL

Melting points were obtained on a Rapido Boetius apparatus and are uncorrected. ^{1}H nmr spectra were recorded on a Bruker Avance (500 MHz) or on a Varian Gemini 300 instrument (300 MHz). ^{13}C nmr spectra were recorded on a Bruker Avance (125 MHz) or on a Varian Gemini 300 (75 MHz) instrument. Mass spectra (EI, 70 eV) were measured on a MS-50 A.E.I. spectrometer. Thin-layer chromatography was carried out using aluminum sheets coated with silica gel 60 F_{254} (Merck). Chromatograms were detected by UV fluorescence and visualized with $FeCl_3$ (in 0.5 *M* hydrochloric acid), or anisaldehyde / ethanol / acetic acid / concentrated sulfuric acid (1:50:20:2) followed by heating, or iodine / potassium iodide (in ethanol/ water 1:10) and 2 *M* hydrochloric acid. Column chromatography was performed with silica gel 60 G (Merck), and fractions were analyzed by thin-layer chromatography using the same solvent. Alkylation of diethyl acetamidomalonate was carried out according to standard procedures [12].

5-Acetamido-5-methyl-1-phenylbarbituric Acid (**2a**).

Diethyl 2-acetamido-2-methyl-malonate **1a** (9.25 g, 40 mmoles) and phenylurea (5.45 g, 40 mmoles) were added to a 0.24 *M* solution of sodium ethoxide in anhydrous ethanol (200 ml, 1.2 equivalents). The mixture was refluxed for 3 hours and evaporated under reduced pressure. The yellow oily residue was dissolved in water (120 ml) and acidified to pH 2-3 by dropwise addition of cold 2 *M* hydrochloric acid. After cooling for 2 days at 5 °C, the crude product precipitated as a mixture of 5-methyl-5-phenylcarbamoylhydantoin (**4a**) and 5-acetamido-5-methyl-1-phenylbarbituric acid (**2a**) as it was confirmed by spectral data (^{1}H nmr, ^{13}C nmr) and thin-layer chromatography. Recrystallization from ethanol yielded 3.54 g (32 %) of **2a** as white crystals, mp > 250 °C (dec.); ^{1}H nmr (DMSO-d_6, 500 MHz): δ 1.65 (s, 3H, 5-CH_3), 1.86 (s, 3H, $COCH_3$), 7.18-7.21 (m, 2H, H-2'), 7.38-7.49 (m, 3H, H-3', H-4'), 9.20 (s, 1H, N*H*$COCH_3$), 11.73 (s, 1H, NH); ^{13}C nmr (DMSO-d_6, 125 MHz): δ 21.24 (CO*C*H_3), 22.33 (CH_3), 59.05 (C-5), 128.69 (C-4'), 128.88, 129.10 (C-2', C-3'), 135.01 (C-1'), 149.72 (C-2), 170.29, 170.31, 170.98 (C-4, C-6, *C*OCH_3); ms: m/z 275 (95 %, M^+), 233 (10 %, $M^+ - CH_2CO$), 114 (82 %, $M^+ - CH_2CO - C_6H_5NCO$), 93 (100 %, $C_6H_7N^+$).

Anal. Calcd. for $C_{13}H_{13}N_3O_4$: C, 56.73; H, 4.76; N, 15.27. Found: C, 56.61; H, 5.06; N, 14.94.

5-Acetamido-5-ethyl-1-phenylbarbituric Acid (**2b**).

Diethyl 2-acetamido-2-ethylmalonate (19.62 g, 80 mmoles) and phenylurea (10.90 g, 80 mmoles) were added to a 0.24 *M* solution of sodium ethoxide in anhydrous ethanol (200 ml, 1.2 equivalents). The mixture was refluxed for 3 hours and evaporated *in vacuo*. The yellow oily residue was dissolved in water (150 ml) and acidified to pH 2-3 by dropwise addition of cold 2 *M* hydrochloric acid. After cooling overnight at 5 °C, the precipitate was isolated by filtration and dried. The crude product was identified as a mixture of 5-ethyl-5-phenylcarbamoylhydantoin (**4b**) and 5-acetamido-5-ethyl-1-phenylbarbituric acid (**2b**) by means of nmr and thin-layer chromatography. It was recrystallized from ethanol to give 10.30 g (45 %) of **2b** as white crystals, mp > 250 °C (dec.); ^{1}H nmr (DMSO-d_6, 500 MHz): δ 0.97 (t, 3H, J = 7.53 Hz, CH_2CH_3), 1.87 (s, 3H, $COCH_3$), 2.02 (q, 2H, J = 7.53 Hz, CH_2), 7.14-7.17 (m, 2H, H-2'), 7.39-7.50 (m, 3H, H-3', H-4'), 9.11 (s, 1H, N*H*$COCH_3$), 11.83 (s, 1H, NH); ^{13}C nmr (DMSO-d_6, 125 MHz): δ 7.83 (CH_2CH_3), 21.24 (CO*C*H_3), 29.71 (CH_2CH_3), 63.10 (C-5), 128.74 (C-4'), 129.22, 129.76 (C-2', C-3'), 134.90 (C-1'), 149.86 (C-2), 169.65, 170.28, 170.42 (C-4, C-6, *C*OCH_3); ms: m/z 289 (50 %, M^+), 127 (29 %, $M^+ - CH_3CO - C_6H_5NCO$), 119 (72 %, $C_6H_5NCO^+$), 93 (100 %, $C_6H_7N^+$).

Anal. Calcd. for $C_{14}H_{15}N_3O_4$: C, 58.13; H, 5.23; N, 14.53. Found: C, 58.05; H, 5.27; N, 14.51.

5-Acetamido-1-phenylbarbituric Acid (**2c**).

Diethyl acetamidomalonate **1c** (8.68 g, 40 mmoles) and phenylurea (5.45 g, 40 mmoles) were added to a 0.24 *M* solution of sodium ethoxide in anhydrous ethanol (200 ml, 1.2 equivalents). The mixture was refluxed for 7 hours meanwhile a white precipitate was formed. The mixture was cooled, diluted with ice-water (50 ml), and the solution was acidified with 6 *M* hydrochloric acid. The precipitate was separated by suction filtration, washed with water and recrystallized from acetic acid to obtain 8.4 g (80 %) of **2c**, mp 252-256 °C; ^{1}H nmr (DMSO-d_6, 300 MHz): δ 1.94 (s, 3H, CH_3), 5.25 (d, 1H, J = 6.5 Hz, H-5), 7.19-7.25 (m, 2H, H-2'), 7.43-7.53 (m, 3H, H-3', H-4'), 9.01 (d, 1H, J = 6.5 Hz, N*H*$COCH_3$), 11.75 (s, 1H, NH); ^{13}C nmr (DMSO-d_6, 75 MHz): δ 22.24 (CH_3), 55.66 (C-5), 129.20 (C-4'), 129.44, 129.70 (C-2', C-3'), 135.69 (C-1'), 151.10 (C-2),

167.22, 167.72, 170.83 (C-4, C-6, *C*OCH$_3$); ms: m/z 261 (58 %, M$^+$), 219 (100 %, M$^+$ – CH$_2$CO), 119 (17 %, C$_6$H$_5$NCO$^+$), 93 (17 %, C$_6$H$_7$N$^+$).

Anal. Calcd. for C$_{12}$H$_{11}$N$_3$O$_4$ × 0.1 H$_2$O: C, 54.79; H, 4.29; N, 15.98. Found: C, 54.76; H, 4.48; N, 15.70.

5-Methyl-5-phenylcarbamoylhydantoin (**4a**).

Diethyl 2-acetamido-2-methylmalonate **1a** (9.25 g, 40 mmoles) and phenylurea (5.45 g, 40 mmoles) were added to a solution of sodium (3.7 g, 160 mmol, 4 equivalents) in anhydrous butanol (200 ml). The mixture was refluxed for 5 hours under an argon atmosphere. Most of the solvent was removed under reduced pressure. Water (80 ml) was added, the mixture was stirred for 2 minutes, and kept at room temperature for 30 min. The organic layer was removed, and the aqueous phase was extracted with ethyl acetate (3 × 20 ml) and then acidified with 2 *M* hydrochloric acid. The precipitate was collected by filtration and dried to give of 2.9 g (31 %) of **4a**, mp 159-162 °C (ethanol), ref 154-156 °C [4]; ^{1}H nmr (DMSO-d$_6$, 500 MHz): δ 1.61 (s, 3H, CH$_3$), 7.11-7.17 (m, 1H, H-4'), 7.30-7.38 (m, 2H, H-3'), 7.64-7.68 (m, 2H, H-2'), 8.38 (s, 1H, PhN*H*), 9.76, 10.95 (each s, total 2H, NH); ^{13}C nmr (DMSO-d$_6$, 125 MHz): δ 21.67 (CH$_3$), 66.63 (C-5), 120.82 (C-2'), 124.26 (C-4'), 128.67 (C-3'), 138.32 (C-1'), 156.87 (C-2), 165.62 (*C*ONHPh), 173.74 (C-4).

5-Ethyl-5-phenylcarbamoylhydantoin (**4b**) [4].

Diethyl 2-acetamido-2-ethylmalonate **1b** (0.98 g, 4 mmoles) and phenylurea (0.55 g, 4 mmoles) were added to a 0.8 *M* solution of sodium ethoxide in anhydrous ethanol (20 ml, 4 equivalents). The mixture was stirred in a sealed tube at 120 °C for 5 hours under an argon atmosphere. The yellow suspension was evaporated to dryness. The oily residue was dissolved in water (20 ml), and charcoal and silica gel were added to the solution. After stirring for 5 minutes and filtration, the filtrate was acidified to pH 2-3 by dropwise addition of cold 2 *M* hydrochloric acid. After cooling overnight, the crude product was collected by filtration to give 0.42 g (42 %) of **4b** as colorless crystals; ^{1}H nmr (DMSO-d$_6$, 500 MHz): δ 0.83 (t, 3H, J = 7.35 Hz, CH$_2$C*H*$_3$), 1.97-2.13 (m, 2H, C*H*$_2$CH$_3$), 7.06-7.11 (m, 1H, H-4'), 7.28-7.33 (m, 2H, H-3'), 7.61-7.63 (m, 2H, H-2'), 8.37 (s, 1H, PhN*H*), 9.64, 10.93 (each s, total 2H, NH); ^{13}C nmr (DMSO-d$_6$, 125 MHz): δ 7.71 (CH$_2$*C*H$_3$), 27.69 (*C*H$_2$CH$_3$), 70.87 (C-5), 120.83 (C-2'), 124.28 (C-4'), 128.67 (C-3'), 138.23 (C-1'), 157.10 (C-2), 165.02 (*C*ONHPh), 173.87 (C-4).

1-Acetyl-2,2-bis(ethoxycarbonyl)pyrrolidine (**5**).

A mixture of diethyl acetamidomalonate **1c** (8.68 g, 40 mmoles), 1,3-dibromopropane (16.15 g, 8.12 mL, 80 mmoles), potassium carbonate (5.53 g, 40 mmoles) and benzyltriethylammonium chloride (300 mg) in anhydrous acetonitrile (30 ml) was stirred at reflux for 14 hours. The resulting suspension was filtrated, and the solvent was removed under reduced pressure to provide a yellow oily residue. The crude product was purified by column chromatography (eluent, dichloromethane/ethyl acetate 1:2 to 1:4) to afford 5.37 g (52 %) of **5** as an yellow oil; ^{1}H nmr (deuteriochloroform, 500 MHz): δ 1.26 (t, 6H, J = 0.83 Hz, CH$_2$C*H*$_3$), 1.92-1.99 (m, 2H, 4-H), 2.07 (s, 3H, COCH$_3$), 2.45 (t, 2H, J = 7.1 Hz, H-3), 3.61 (t, 2H, J = 6.9 Hz, H-5), 4.16-4.28 (m, 4H, C*H*$_2$CH$_3$); ^{13}C nmr (deuteriochloroform, 125 MHz): δ 13.96 (CH$_2$*C*H$_3$), 22.40 (CO*C*H$_3$), 24.16 (C-4), 36.26 (C-3), 48.26 (C-5), 61.97 (*C*H$_2$CH$_3$), 72.30 (C-2), 168.69 (CO-O), 169.22 (CO-N); ms: m/z 257 (2 %, M$^+$), 185 (10 %, M$^+$ – C$_3$H$_4$O$_2$), 142 (35 %, M$^+$ - C$_3$H$_4$O$_2$ – CH$_3$CO), 112 (42 %, M$^+$ – C$_6$H$_7$O$_4$), 70 (100 %, C$_4$H$_8$N$^+$).

1-Acetyl-7-phenyl-triaza[4,5]decane-6,8,10-trione (**6**).

1-Acetyl-2,2-bis(ethoxycarbonyl)pyrrolidine **5** (1.54 g, 6 mmoles) and phenylurea (0.82 g, 6 mmoles) were added to a 0.24 *M* solution of sodium ethoxide in anhydrous ethanol (30 ml, 1.2 equivalents). The mixture was refluxed for 5 hours. Water (25 ml) was added to the resulting suspension, followed by filtration. The filtrate was acidified to pH 1-3 by dropwise addition of cold 2 *M* hydrochloric acid. The crude product was isolated by extraction of the aqueous solution with ethyl acetate (5 × 15 ml). The combined organic layers were dried (sodium sulfate) and evaporated to dryness. The crude product was recrystallized from ethanol to yield 180 mg (10 %) of the spirobarbituric acid **6** as white crystals, mp 234-236 °C; ^{1}H nmr (DMSO-d$_6$, 500 MHz): δ 2.01 (s, 3H, CH$_3$), 2.08-2.16 (m, 2H, H-3), 2.32-2.47 (m, 2H, H-4), 3.74 (t, 2H, J = 6.7 Hz, H-2), 7.40-7.48 (m, 5H, phenyl), 11.84 (s, 1H, NH); ^{13}C nmr (DMSO-d$_6$, 125 MHz): δ 21.52 (CH$_3$), 24.93 (C-3), 37.54 (C-4), 48.71 (C-2), 67.93 (C-5), 128.77 (C-4'), 128.92, 129.16 (C-2', C-3'), 134.90 (C-1'), 149.96 (C-8), 168.78, 169.95, 170.42 (C-6, C-10, *C*OCH$_3$); ms: m/z 301 (100 %, M$^+$), 258 (58 %, M$^+$ – CH$_3$CO), 139 (16 %, M$^+$ – CH$_3$CO – C$_6$H$_5$NCO), 119 (24 %, C$_6$H$_5$NCO$^+$), 93 (25 %, C$_6$H$_7$N$^+$).

Anal. Calcd. for C$_{15}$H$_{15}$N$_3$O$_4$ × 0.2 H$_2$O: C, 59.09; H, 5.09; N, 13.78. Found: C, 59.04; H, 5.30; N, 13.41.

7a-Phenylcarbamoyl-tetrahydro-1*H*-pyrrolo[1,2-*c*]imidazole-1,3(2*H*)-dione (**8**).

1-Acetyl-2,2-bis(ethoxycarbonyl)pyrrolidine **5** (1.54 g, 6 mmoles) and phenylurea (0.82 g, 6 mmoles) were added to a 1.3 *M* solution of sodium ethoxide in anhydrous ethanol (18.5 ml, 4 equivalents). The mixture was stirred in a sealed tube at 120 °C for 8 hours under an argon atmosphere. The solution was evaporated to dryness. A small amount of water was added, and insoluble material was removed by filtration. The filtrate was acidified to pH 2-3 by dropwise addition of cold 2 *M* hydrochloric acid, and the solution was extracted with ethyl acetate (5 × 20 ml). The combined organic layers were dried (sodium sulfate) and the solvent was removed under reduced pressure. The oily residue was purified by column chromatography (eluent, dichloromethane/ethyl acetate 1:4). Ethyl *N*-phenylcarbamate was isolated as the fastest leaving fraction (220 mg, retention factor 0.84, yellow oil); ^{1}H nmr (DMSO-d$_6$, 500 MHz): δ 1.23 (t, 3H, J = 7.1 Hz, CH$_3$), 4.11 (q, 2H, J = 7.1 Hz, CH$_2$), 6.94-6.98 (m, 1H, H-4'), 7.23-7.27 (m, 2H, H-3'), 7.44-7.45 (m, 2H, H-2'), 9.54 (s, 1H, NH); ^{13}C nmr (DMSO-d$_6$, 125 MHz): δ 14.64 (CH$_3$), 60.20 (CH$_2$), 118.32 (C-2'), 122.39 (C-4'), 128.81 (C-3'), 139.37 (C-1'), 153.68 (CO). Compound **8** (60 mg, retention factor 0.65, yellow oil) was obtained in 4 % yield; ^{1}H nmr (DMSO-d$_6$, 500 MHz): δ 1.87-2.06 (m, 2H, H-6), 2.60-2.64 (m, 1H, H-7), 3.15-3.19 (m, 1H, H-7), 3.57-4.13 (m, 2H, H-5), 7.07-7.10 (m, 1H, H-4'), 7.29-7.31 (m, 2H, H-3'), 7.64-7.66 (m, 2H, H-2'), 9.91 (s, 1H, NH); ^{13}C nmr (DMSO-d$_6$, 125 MHz): δ 26.12 (C-6), 30.94 (C-7), 45.25 (C-5), 77.29 (C-7a), 120.72 (C-2'), 124.31 (C-4'), 128.65 (C-3'), 138.27 (C-1'), 160.58 (C-3), 164.64 (*C*ONHPh), 171.78 (C-1).

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