# Reaction of a Zwitterionic Pyridinium Ylide with *N,N*-Dimethylaniline

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1,3-Dimethyl-2,4,6-trioxo-5-pyridinomethyl-1,3-perhydrodiazin-5-ylpyridinium ylide (**3**) reacts with *N,N*-dimethylaniline to give 5-((1,3-dimethyl-2,4,6-trioxo-hexahydropyrimidin-5-yl)methyl)-5-(4-(dimethylamino)benzyl)-1,3-dimethylpyrimidine-2,4,6(1*H*3*H*5*H*)-trione (**6**) in good yield. The crystal structure of **6** is reported.

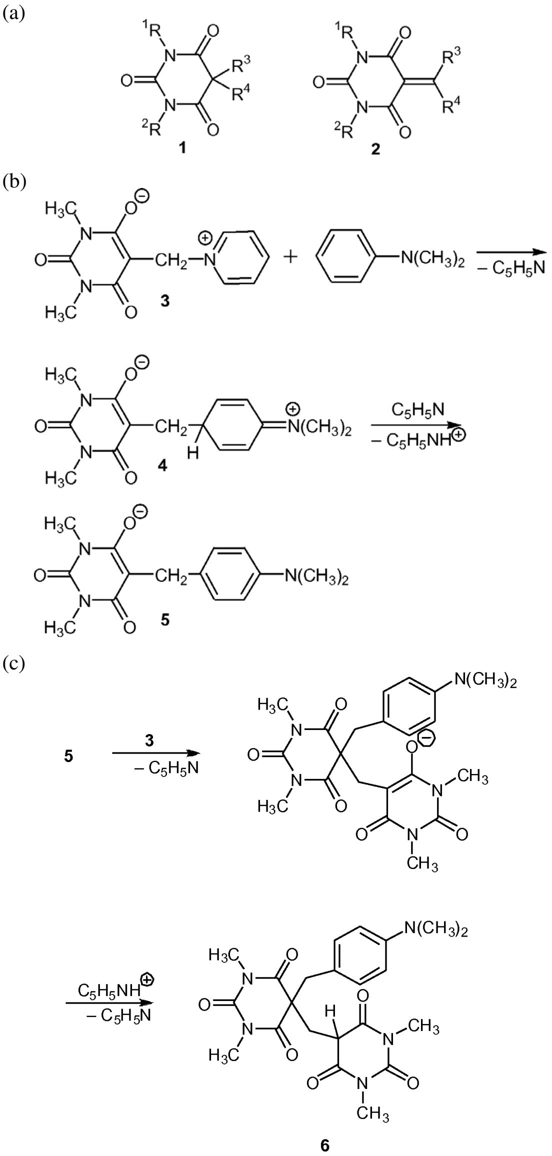
*Key words:* Heterocycles, Barbituric Acid,
Crystal Structure

There has been much interest in barbituric acid derivatives (**1**) in the past years owing to their potential application as drugs [1, 2]. Catalytic hydrogenation of 5-methylenebarbituric acid derivatives (**2**) seems to offer a useful access to **1** [3] in addition to methods mentioned formerly [1, 4]. Recently, we reported on the synthesis of the zwitterionic pyridinium compound **3** and its substitution reactions [5].

Surprisingly, it has now been found that the reaction of **3** with *N,N*-dimethylaniline does not stop with the formation of the zwitterionic compound **4** and its anion **5**. Apparently, the enolate **5** is sufficiently nucleophilic to attack a second molecule of **3** to give the final product **6** in good yield (Scheme 1).

The crystal structure analysis of **6** (Table 1, Fig. 1) reveals the presence of a central barbituric ring connected to both an aniline and an additional barbituric ring by methylene bridges. Interestingly, the "terminal" barbituric ring also adopts a diketo structure which underlines the C-basicity of the enolate fragment. Bond lengths and angles are in the expected range (see Table 2).

In summary, our results confirm the suitability of the easily prepared pyridine adduct **3** as starting compound for the synthesis of barbituric acid derivatives **1**. We will continue our investigations about pyridine substitution in **3** and report on our results in due course.



Scheme 1.

## Experimental Section

All experiments were performed in purified solvents under argon. The pyridine adduct **3** was obtained according to a published procedure [5].

Table 1. Crystal data and structure refinement for $C_{22}H_{27}N_5O_6$ (**6**).

| | |
|---|---|
| Empirical formula | $C_{22}H_{27}N_5O_6$ |
| Formula weight, g mol$^{-1}$ | 457.49 |
| Temperature, K | 173(2) |
| Wavelength; $\lambda$, Å | Mo$K_\alpha$; 0.71073 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| $a$, Å | 12.1221(9) |
| $b$, Å | 9.287(1) |
| $c$, Å | 20.090(2) |
| $\beta$, deg | 101.787(6) |
| $V$, Å$^3$ | 2214.1(3) |
| $Z$ | 4 |
| Density, g cm$^{-3}$ | 1.37 |
| $\mu$(Mo$K_\alpha$), mm$^{-1}$ | 0.1 |
| $F$(000), e | 968 |
| $\Theta$ range for data collection, deg | 3.09 – 26.36 |
| $hkl$ ranges | ±15, ±11, ±25 |
| Reflections collect. / indep. / $R_{\text{int}}$ | 30767 / 4515 / 0.098 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 4515 / 0 / 407 |
| $R1$ / w$R2$ [$I \geq 2\ \sigma(I)$] | 0.0520 / 0.1048 |
| $R1$ / w$R2$ (all data) | 0.0677 / 0.1111 |
| Goodness-of-fit on $F^2$ | 1.151 |
| $\Delta\rho$ (max / min), e Å$^{-3}$ | +0.267 / −0.207 |

### *$C_{22}H_{27}N_5O_6$ (6)*

To a solution of **3** (2.2 g, 8.9 mmol) in dichloromethane (20 mL) *N,N*-dimethylaniline (0.62 g, 4.9 mmol) was added. The mixture was stirred at r. t. for 24 h. The solvent was removed *in vacuo* to give 0.79 g (70 %) **6** after recrystallization from dichloromethane/diethyl ether. – $^1$H NMR ($CDCl_3$): $\delta$ = 2.75 (s, 2 H, $4_{Ph}$-$CH_2$), 2.83 (s, 6 H, $NMe_2$), 2.95 (s, 2 H, 5′-$CH_2$), 3.01 (s, 6 H, 1′,3′-$CH_3$), 3.15 (s, 6 H, 1,3-$CH_3$), 3.65 (s, 1 H, 5′-H), 6.48 – 6.69 (m, 4 H, $C_6H_4$). – $^{13}$C NMR ($CDCl_3$): $\delta$ = 28.2 (1,3-$CH_3$), 28.5 (1′,3′-$CH_3$), 33.7 ($4_{Ar}$-$CH_2$), 40.3 ($NMe_2$), 44.6 ($C^{5'}$), 49.5 $C^5$), 56.1 (5′-$CH_2$), 111.8 ($C^{2,6}{}_{Ar}$), 119.9 ($C^4{}_{Ar}$), 129.7 ($C^{3,5}{}_{Ar}$), 150.3 ($C^1{}_{Ph}$), 150.6 ($C^2$), 151.2 ($C^{2'}$), 168.3 ($C^{4',6'}$), 170.9 ($C^{4,6}$). – MS (FAB): *m/z* (%) = 457 (11) $[M–H]^+$, 288 (15) $[M–BCH_3]^+$. – Elemental analysis for $C_{22}H_{27}N_5O_6$ (457.48): calcd. C 57.76, H 5.95, N 15.31; found C 57.41, H 6.19, N 15.12.

Table 2. Selected bond lengths (Å) and angles (deg) for $C_{22}H_{27}N_5O_6$ (**6**).

| | | | |
|---|---|---|---|
| C(1)–C(6) | 1.503(3) | C(14)–N(15) | 1.382(2) |
| C(1)–C(2) | 1.505(3) | N(15)–C(16) | 1.381(3) |
| C(1)–C(12) | 1.556(3) | C(16)–O(21) | 1.208(2) |
| C(2)–O(7) | 1.209(2) | C(16)–N(17) | 1.393(3) |
| C(2)–N(3) | 1.379(2) | N(17)–C(18) | 1.371(2) |
| N(3)–C(4) | 1.390(2) | C(18)–O(23) | 1.215(2) |
| C(4)–O(9) | 1.205(2) | C(24)–C(25) | 1.507(3) |
| C(4)–N(5) | 1.394(2) | C(25)–C(26) | 1.390(3) |
| N(5)–C(6) | 1.372(2) | C(25)–C(30) | 1.391(3) |
| C(6)–O(11) | 1.216(2) | C(26)–C(27) | 1.383(3) |
| C(12)–C(13) | 1.537(2) | C(27)–C(28) | 1.404(3) |
| C(13)–C(18) | 1.512(3) | C(28)–N(31) | 1.377(3) |
| C(13)–C(14) | 1.514(3) | C(28)–C(29) | 1.402(3) |
| C(13)–C(24) | 1.589(3) | C(29)–C(30) | 1.384(3) |
| C(14)–O(19) | 1.210(2) | | |
| C(13)–C(12)–C(1) | 116.4(2) | C(6)–C(1)–C(2) | 115.1(2) |
| C(12)–C(13)–C(24) | 106.8(2) | C(6)–C(1)–C(12) | 111.6(2) |
| C(25)–C(24)–C(13) | 115.1(2) | C(2)–C(1)–C(12) | 106.1(2) |
| C(33)–N(31)–C(32) | 117.6(2) | | |

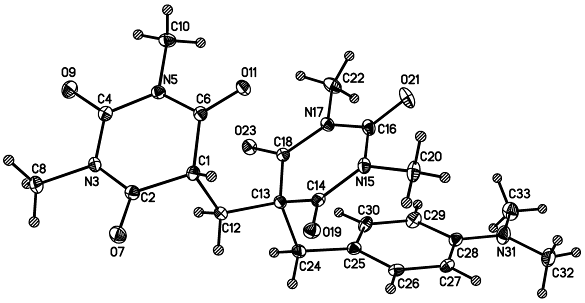


Fig. 1. Molecular structure of $C_{22}H_{27}N_5O_6$ (**6**) in the crystal.

CCDC 743774 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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