Tetrahedron Vol 46, No 11, pp 3781-3788, 1990
Printed in Great Britain

0040-4020/90 $3 00+ 00
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PHOTOCHEMICAL REACTIONS OF BARBITURIC ACIDS

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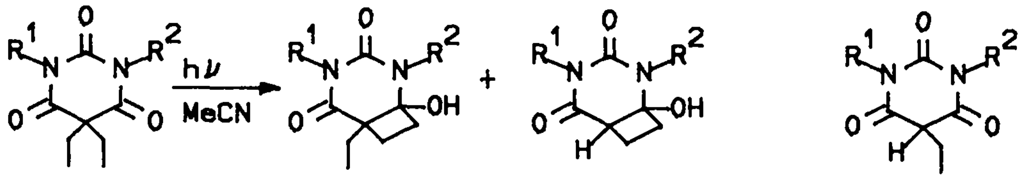
(*Received in Japan* 12 *December* 1989)

Abstract - Photochemical reaction of barbital (**1a**) and its derivatives gave Norrish type II reaction products. Their photochemical reactivities is discussed in comparison with those of other nitrogen-containing carbonyl compounds.

Barbituric acids (barbiturates) are well-known for their hypnotic and sedative effects, and have been studied extensively.[1] Their photochemical reactivity is also of interest in relation to that of extensively investigated cyclic imides[2] or acylureas[3], since barbituric acid possesses a chromophore which consists of two nitrogen atoms and three carbonyl groups and can be regarded as a cyclic diacylurea. Otsuji et al. reported photochemical hydrolysis of barbital (1a, 5,5-diethylbarbituric acid) in aqueous solutions,[4] and Barton et al. recently reported Norrish type I reaction (α-cleavage) of the anion of **1a**[5] In this paper, we report photochemical hydrogen abstraction of **1a** and its derivatives, and discuss their photochemical reactivities in connection with those of other nitrogen-containing carbonyl compounds.

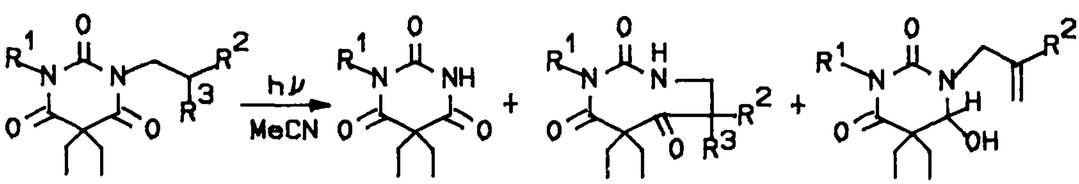
In general, photoreactions of barbituric acids are not clean, and many unidentified by-products are formed in every case. When **1a** in acetonitrile was irradiated with a low pressure mercury lamp, two bicyclic compounds (**2a** and **3a**) were obtained. The structure of **2a** was determined on the basis of the spectral data and elemental analysis. The IR spectrum of **2a** exhibited a carbonyl absorption (1697 cm^{-1}) characteristic of a dihydrouracil structure. The ^{13}C-NMR spectrum showed the presence of a methyl group (δ 10.1), three methylene groups (δ 26.0, 26.3, and 35.6), two quaternary carbons (δ 52.2 and 82.8), and two carbonyl groups (δ 153.8 and 175.9). The structure of **3a** was determined in a similar manner. Irradiation of N,N'-dimethylbarbital (1b) gave a similar result, but a minor product (3b) was not completely purified. Photoreaction of N-methylbarbital (1c, metharbital) also gave 2c and 3c. In this case, each of them was a mixture of two isomers (R^1=H, R^2=Me and R^1=Me, R^2=H), which could not be separated. Formation of 2 can easily be explained in terms of Norrish type II cyclization, whereas 3 is presumed to be produced via type II cleavage and subsequent type II cyclization of the resulting 5-ethylbarbituric acid (4) although 4 was not isolated. The possibility that 3 was formed by type II elimination of 2 was excluded since irradiation of 2a did not yield 3a.



1 2 3 4

	2	3
a: R^1=R^2=H	28%	16%
b: R^1=R^2=Me	34%	14%
c: R^1=H, R^2=Me	36%	8%

When N-propylbarbital (1d) was irradiated in acetonitrile, barbital (1a), a ring-expansion product (5d), and an intramolecular disproportionation product (6d) were obtained. The structure of 5d was determined by spectral data and elemental analysis. The ^{1}H-NMR spectrum showed the signal of the 8-methyl group at δ 1.13 (d). The ^{13}C-NMR spectrum showed the presence of a ketone carbonyl (δ 209.5) in addition to two carbonyl groups of the acylurea system (δ 156.3 and 173.6). The structure of 6d



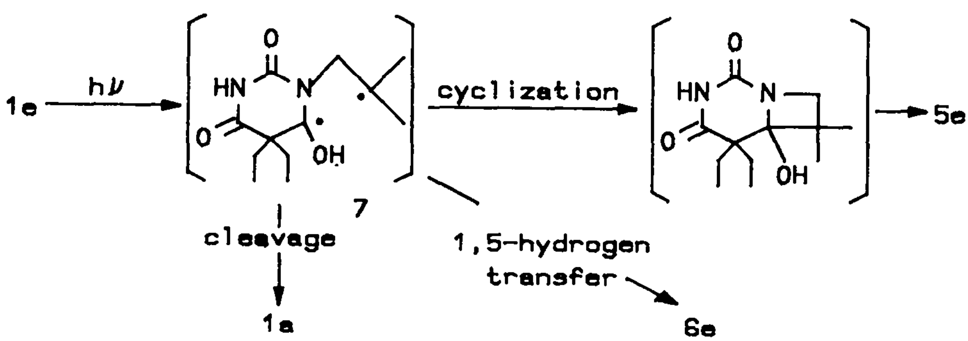
1 1a or 1c 5 6

	1a or 1c	5	6
d: R^1=R^2=H, R^3=Me	17% (1a)	12%	22%
e: R^1=H, R^2=R^3=Me	7% (1a)	17%	26%
f: R^1=R^3=Me, R^2=H	14% (1c)	19%	13%
g: R^1=R^2=H, R^3=Ph	35% (1a)	0%	-
h: R^1=Me, R^2=H, R^3=Ph	36% (1c)	0%	-

was also determined on the basis of spectral data and elemental analysis. Photoreaction of N-isobutylbarbital (1e) and N-methyl-N'-propylbarbital

(**1f**) gave similar results, whereas that of N-(2-phenylethyl)barbitals (**1g** and **1h**) yielded only dealkylation products (**1a** and **1c**). Formation of styrene in the photolysis of **1g** was also confirmed (VPC and NMR).

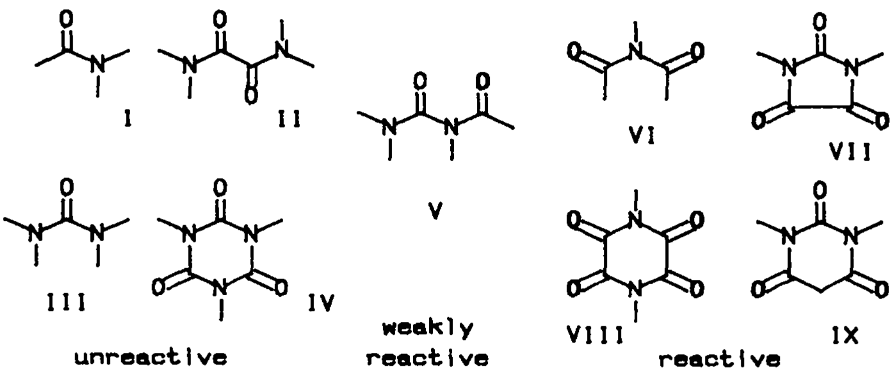
These dealkylation products are apparently produced via the type II elimination. The formation of 5 and 6 is also explainable in terms of the type II process. Cyclization of the diradical (7) followed by ring opening via cleavage of the C-N bond gives 5, whereas 1,5-hydrogen transfer of 7 affords 6. It is known that cyclic imides undergo analogous reactions.[2] The absence of the products analogous to 2 formed by hydrogen abstraction from the 5-ethyl groups in the reactions of **1d-h** is explainable by the higher reactivity of the methylene hydrogens toward abstraction than that of methyl hydrogens.[6] It is also conceivable that hydrogen abstraction from the N-alkyl groups is sterically more favorable than that from the 5-ethyl groups.



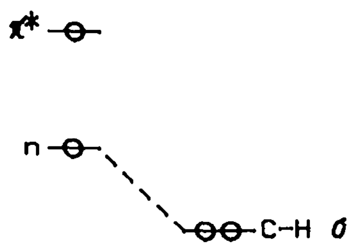
The spectrum of barbital in acetonitrile showed an absorption at 260-270 nm as a shoulder which was presumed to be the n,π^* absorption on the basis of the extinction coefficient (ε=50). The multiplicities of the reactive excited states in the photoreactions of **1a-h** could not be determined since suitable sensitizers or quenchers could not be found.

Photochemical Reactivities of Nitrogen-Containing Carbonyl Compounds. The barbituric acids undergo Norrish type II reaction even when γ-hydrogens are methyl hydrogens whose reactivity toward abstraction is quite low.[6] These compounds therefore possess photochemical reactivities comparable to those of imides and ketones. Figure 1 summarizes the photochemical reactivities of a variety of nitrogen-containing carbonyl compounds. Amides,[2b] oxamides,[7] ureas,[7] and isocyanurates[7] are photochemically unreactive. Acylureas possess weak photochemical reactivity: they undergo intramolecular hydrogen abstraction only when hydrogens to be abstracted are strongly activated by substituents.[3b,c] Meanwhile, imides,[2] imidazolidinetriones,[8,9] piperazinetetrones,[10] and barbituric acids exhibited photochemical reactivities comparable to ketones. These results indicate that the elecron-donating nitrogen atoms make the carbonyl groups photochemically unreactive and that the reactivity of the carbonyl groups survives when the electron-donating effects of the nitrogen atoms are weakened by the introduction of another carbonyl group.[11]

Figure 1. Photochemical Reactivities of Nitrogen-Containing Carbonyl Compounds.



These facts are reasonably explained on the basis of the frontier orbital theory. It is well-known that the reactivities of the n,π* states of carbonyl compounds resemble those of alkoxy radicals, and this resemblance is due to the fact that both species possess a singly occupied orbital (SOMO) localized around the oxygen atom.[12] The interaction between this nonbonding SOMO and a C-H orbital plays crucial roles in hydrogen abstraction by these species.[13a] The electron-donating nitrogen atoms directly bonded to the carbonyl groups of the compounds (I-IV) should raise the energies of the SOMOs[13b] and, in other words, make the carbonyl n,π* states less electrophilic.[14] The energy difference between the nonbonding SOMO and the C-H orbital thus becomes large, and hence the interaction between these orbitals becomes weak. Accordingly, the compounds (I-IV) do not undergo photochemical hydrogen abstraction. On the other hand, the electron donating effects of the nitrogens in the compounds (V-IX) are weak owing to the electron-withdrawing effects of the additional carbonyl groups. These compounds therefore exhibit photochemical reactivities similar to those of ketones. In conclusion, barbituric acids were found to possess photo chemical reactivities analogous to those of imides. This fact can be rationalized in terms of the weak electron-donating effects



of the nitrogen atoms of these compounds to the adjacent carbonyl groups.

Experimental

Melting points were taken on a Yanagimoto Micro Melting Point apparatus and are uncorrected. IR spectra were measured on a JASCO IRA-1 Infrared spectrophotometer with $CHCl_3$ as a solvent unless otherwise noted. ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL FX-90Q or FX-100 spectrometer with $CDCl_3$ as a solvent unless otherwise noted. A Rayonet photochemical reactor (RPR 2537A) was used as an irradiation source. Elemental analyses were performed by a Perkin-Elmer Model 240 elemental analyzer.

Materials. Barbital (**1a**) is commercially available. Dimethylbarbital (**1b**),[15] methylbarbital (**1c**),[16] and propylbarbital (**1d**)[17] were prepared according to the literature. Other compounds (**1e-h**) were synthesized as in the case of **1d** from **1a** or **1c**.

5,5-Diethyl-1-(2-methylpropyl)barbituric acid (1e): mp 107-108 °C; IR 3500, 1720, 1690 cm^{-1}; ^{1}H NMR δ 0.86 (t, 6H, J=7.3Hz, Me), 0.94 (d, 6H, J=6.4Hz, Me), 1.8-2.2 (m, 1H, methine), 2.05 (q, 4H, J=7.3Hz, CH_2), 3.76 (d, 2H, J=7.4Hz); ^{13}C NMR δ 9.5 (q), 20.0 (q), 27.1 (d), 32.5 (t), 48.2 (t), 58.2 (s), 150.6 (s), 172.4 (s), 172.7 (s). Anal. Calcd for $C_{12}H_{20}N_2O_3$: C, 59.98; H, 8.39; N, 11.66. Found: C, 59.91; H, 8.56; N, 11.71.

5,5-Diethyl-1-methyl-3-propylbarbituric acid (1f): bp 50°C/10^{-3} torr (bath temp.); IR 1745, 1670 cm^{-1}; ^{1}H NMR δ 0.77 (t, 6H, J=7.3Hz, Me), 0.96 (t, 3H, J=6.9Hz, Me), 1.4-1.8 (m, 2H, CH_2), 2.03 (q, 4H, J=7.3Hz, CH_2), 3.34 (s, 3H, NMe), 3.8-4.0 (m, 2H, CH_2); ^{13}C NMR δ 9.5 (q), 11.2 (q), 21.4 (t), 28.3 (q), 33.0 (t), 43.6 (t), 58.2 (s), 151.0 (s), 171.6 (s), 172.0 (s). Anal. Calcd for $C_{12}H_{20}N_2O_3$: C, 59.98; H, 8.39; N, 11.66. Found: C, 59.73; H, 8.51; N, 11.53.

5,5-Diethyl-1-(2-phenylethyl)barbituric acid (1g): mp 145-146°C; IR 3350, 1710, 1680cm^{-1}; ^{1}H NMR δ 0.78 (t, 6H, J=7.3Hz, Me), 2.01 (q, 4H, J=7.3Hz, CH_2), 2.8-3.1 (m, 2H), 4.0-4.3 (m, 2H, NCH_2), 7.28 (s, 5H, Ph), 9.31 (br s, 1H, NH); ^{13}C NMR δ 9.4 (q), 32.4 (t), 34.1 (t), 42.4 (t), 58.2 (s), 126.7 (d), 128.5 (d), 128.9 (d), 137.6 (s), 150.0 (s), 172.1 (s), 172.2 (s). Anal. Calcd for $C_{16}H_{20}N_2O_3$: C, 66.65; H, 6.99; N, 9.72. Found: C, 66.65; H, 7.02; N, 9.69.

5,5-Diethyl-1-methyl-3-(2-phenylethyl)barbituric acid (1h): bp 100-110°C/10^{-3} torr (bath temp.); IR 1740, 1670cm^{-1}; ^{1}H NMR δ 0.72 (t, 6H, J=7.3Hz, Me), 1.99 (q, 4H, J=7.3Hz, CH_2), 2.8-3.0 (m, 2H), 3.33 (s, 3H, NMe), 4.0-4.3 (m, 2H, NCH_2), 7.27 (s, 5H, Ph); ^{13}C NMR δ 9.5 (q), 28.3 (q), 32.9 (t), 34.2 (t), 43.1 (t), 58.2 (s), 126.7 (d), 128.6 (d), 128.9 (d), 137.9 (s), 150.9 (s), 171.5 (s), 171.9 (s). Anal. Calcd for $C_{17}H_{22}N_2O_3$: C, 67.53; H, 7.33; N, 9.26. Found: C, 67.55; H, 7.33; N, 9.15.

General Procedure for the Photolysis of Barbituric acids A solution of 1 (300mg) in 150ml acetonitrile was deaerated with argon and irradiated in a quartz vessel with a low-pressure mercury lamp for 4-10hr. After removal of the solvent, the residue was chromatographed on silica gel followed by distillation or recrystallization.

3,5-Diaza-1-ethyl-6-hydroxybicyclo[4,2,0]octa-2,4-dione (2a): mp 174-178°C dec (in a sealed tube); IR (KBr) 3400, 3200, 3100, 1700cm^{-1}; ^{1}H NMR (CD_3OD) δ 1.00 (t, 3H, J=7.3Hz, Me), 1.6-2.6 (m, 6H); ^{13}C NMR (CD_3OD) δ 10.1 (q), 26.0 (t), 26.3 (t), 35.6 (t), 52.2 (s), 82.8 (s), 153.8 (s), 175.9 (s). Anal. Calcd for $C_8H_{12}N_2O_3$: C, 52.17; H, 6.57; N, 15.21. Found: C, 52.09; H, 6.59; N, 15.15.

3,5-Diaza-6-hydroxybicyclo[4,2,0]octa-2,4-dione (3a): mp (dec) >253°C (in a sealed tube); IR (KBr) 3300, 3200, 3050, 1710, 1650cm^{-1}; ^{1}H NMR (CD_3OD) δ 1.6-2.6 (m, 4H), 3.0-3.1 (m, 1H); ^{13}C NMR δ 19.2 (t), 36.6 (t), 46.6 (d), 80.3 (s), 154.5 (s), 173.0 (s). Anal. Calcd for $C_6H_8N_2O_3$: C, 46.15; H, 5.16; N, 17.94. Found: C, 46.15; H, 5.19; N, 17.57.

3,5-Diaza-1-ethyl-6-hydroxy-N,N'-dimethylbicyclo[4,2,0]octa-2,4-dione (2b): mp 84-85°C; IR 3350, 1700, 1650cm^{-1}; ^{1}H NMR δ 1.00 (t, 3H, J=7.3Hz, Me), 1.6-2.5 (m, 6H), 2.94 (s, 3H, NMe), 3.14 (s, 3H, NMe), 4.78 (br s, 1H, OH); ^{13}C NMR δ 10.1 (q), 24.9 (t), 26.4 (t), 27.7 (q), 28.8 (q), 32.1 (t), 51.1 (s), 84.0 (s), 152.6 (s), 172.5 (s). Anal. Calcd for $C_{10}H_{16}N_2O_3$: C, 56.59; H, 7.60; N, 13.20. Found: C, 56.28; H, 7.62; N, 13.23.

3,5-Diaza-6-hydroxy-N,N'-dimethylbicyclo[4,2,0]octa-2,4-dione (3b) bp 80°C (10^{-3} Torr); IR 3350, 1705, 1660cm^{-1}; ^{1}H NMR δ 1.7-2.5 (m, 4H), 2.95 (s, 3H, NMe), 3.10 (s, 3H, NMe), 3.34 (t, 1H, J=9.5Hz), 5.34 (br s, 1H, OH); ^{13}C NMR δ 18.1 (t), 27.6 (q), 28.6 (q), 33.2 (t), 45.6 (d), 81.3 (s), 152.6 (s), 169.5 (s).

3,5-Diaza-1-ethyl-6-hydroxy-N-methylbicyclo[4,2,0]octa-2,4-dione (2c) was a ca. 1:1 mixture of two isomers; mp 199-201°C dec (in a sealed tube); IR (KBr) 1690, 3200cm^{-1}; characteristic signals of one isomer ^{1}H NMR (CD_3OD) δ 1.00 (t, 3H, J=7.3Hz, Me), 2.91 (s, 3H, NMe); ^{13}C NMR δ 10.5 (q), 26.2 (t), 27.0 (t), 28.1 (q), 33.2 (t), 52.9 (s), 87.1 (s), 153.6 (s), 175.3 (s); another isomer ^{1}H NMR (CD_3OD) δ 0.99 (t, 3H, J=7.3Hz, Me), 3.16 (s, 3H, NMe), 5.94 (br s, 1H), 7.27 (br s, 1H); ^{13}C NMR δ 9.8 (q), 25.6 (t), 25.8 (t), 27.1 (q), 34.9 (t), 51.3 (s), 80.1 (s), 153.3 (s), 173.7 (s). Anal. Calcd for $C_9H_{14}N_2O_3$: C, 54.53; H, 7.12; N, 14.13. Found (for a mixture of the isomers): C, 54.22; H, 7.15; N, 14.09.

3,5-Diaza-6-hydroxy-N-methylbicyclo[4,2,0]octa-2,4-dione (3c) was a ca. 1:1 mixture of two isomers; mp (dec) 173°C (in a sealed tube); IR (KBr) 3450, 3350, 3200, 1710, 1660cm^{-1}; characteristic signals of one isomer ^{1}H NMR (CD_3OD) δ 2.92 (s, 3H, NMe); ^{13}C NMR δ 19.1 (t), 27.8 (q), 34.3 (t), 47.4 (d), 84.6 (s), 154.0 (s), 172.5 (s); another isomer ^{1}H NMR (CD_3OD) δ 3.13 (s, 3H, NMe); ^{13}C NMR δ 19.2 (t), 27.1 (q), 36.4 (t), 46.8 (d), 78.3 (s), 154.6 (s), 171.9 (s). Anal. Calcd for $C_7H_{10}N_2O_3$: C, 49.41; H, 5.92; N, 16.46. Found (for a mixture of the isomers): C, 49.46; H, 6.05; N, 16.47.

1,3-Diaza-5,5-diethyl-7-methylcycloocta-2,4,6-trione (5d): mp 148-149°C; IR 3400, 3250, 1690cm^{-1}; ^{1}H NMR δ 0.75 (t, 3H, J=7.6Hz, Me), 0.80 (t, 3H, J=7.6Hz, Me), 1.13 (d, 3H, J=6.4Hz, Me), 1.5-2.3 (m, 4H, CH_2), 2.8-3.1 and 3.8-4.1 (m, each 1H, NCH_2), 3.25 (sext, 1H, J=6.4Hz, methine), 6.70 (br t, 1H, NH), 8.16 (br s, 1H, NH); ^{13}C NMR δ 8.1 (q), 14.5 (q), 24.8 (t), 25.9 (t), 43.9 (d), 46.3 (t), 65.8 (s), 156.3 (s), 173.6 (s), 209.5 (s). Anal. Calcd for $C_{11}H_{18}N_2O_3$: C, 58.39; H, 8.02; N, 12.38. Found: C, 58.04; H, 8.04; N, 12.34.

1-Allyl-5,5-diethyl-6-hydroxy-1,5-dihydropyrimidine-2,4-dione (6d): mp 143-144°C; IR 3450, 3200, 1680cm^{-1}; ^{1}H NMR (CD_3OD) δ 0.7-1.1 (m, 6H, Me), 1.4-2.4 (m, 4H, CH_2), 3.70 (d of ABq, 1H, J_{ABq}=15.2Hz, J_d=7.4Hz, NCH), 4.46 (d of ABq, 1H, J_{ABq}=15.2Hz, J_d=4.9Hz, NCH), 4.59 (s, 1H, CH), 5.1-5.4 (m, 2H, CH_2=), 5.6-6.1 (m, 1H, =CH-); ^{13}C NMR δ 6.7 (q), 8.4 (q), 10.0 (q), 11.8 (q), 20.6 (t), 23.5 (t), 25.7 (t), 26.3 (t), 26.7 (t), 34.2 (t), 45.2 (t), 48.7 (t), 53.5 (s), 83.2 (d), 87.1 (s), 119.1 (t), 134.5 (d), 153.0 (s), 153.9 (s), 175.5 (s), 176.2 (s). Anal. Calcd for $C_{11}H_{18}N_2O_3$: C, 58.39; H, 8.02; N, 12.38. Found: C, 58.34; H, 8.10; N, 12.28.

1,3-diaza-5,5-diethyl-7,7-dimethylcycloocta-2,4,6-trione (5e): mp 174-175°C; IR 3400, 3200, 1690cm^{-1}; ^{1}H NMR δ 0.71 (t, 6H, J=7.3Hz, Me), 1.20 (s, 6H, Me), 1.4-2.4 (m, 4H), 2.6-3.8 (m, 2H), 7.3 (br t, 1H, NH); ^{13}C NMR δ 7.5 (q), 24.2 (q), 24.9 (t), 50.0 (t), 53.0 (s), 65.1 (s), 156.7 (s), 175.5 (s), 208.1 (s). Anal. Calcd for $C_{12}H_{20}N_2O_3$: C, 59.98; H, 8.39, N, 11.66. Found: C, 59.66; H, 8.40; N, 11.57.

5,5-Diethyl-6-hydroxy-1-(2-isobutenyl)dihydropyrimidine-2,4-dione (6e): mp (dec) 209-211°C (in a sealed tube); IR (KBr) 3350, 1690cm^{-1}; ^{1}H NMR (CD_3OD) δ 0.87 (t, 3H, J=7.3Hz, Me), 0.88 (t, 3H, J=7.3Hz, Me), 1.4-2.4 (m, 4H), 1.77 (s, 3H, Me), 3.89 and 4.25 (ABq, 2H, J=14.9Hz, NCH_2), 4.56 (s, 1H), 5.00 (br s, 2H, =CH_2), 8.12 (br s, 1H, NH); ^{13}C NMR δ 6.8 (q), 8.5 (q), 20.1 (t), 20.6 (q), 25.4 (t), 50.4 (s), 51.1 (t), 82.2 (d), 115.3 (t), 141.3 (s), 153.6 (s), 175.6 (s). Anal. Calcd for $C_{12}H_{20}N_2O_3$: C, 59.98; H, 8.39; N, 11.66. Found: C, 59.72; H, 8.50; N, 11.63.

1,3-Diaza-5,5-diethyl-3,7-dimethylcycloocta-2,4,6-trione (5f): mp 133-134°C; IR 3400, 1700, 1660cm^{-1}; ^{1}H NMR δ 0.71 (t, 3H, J=7.6Hz, Me), 0.74 (t, 3H, J=7.6Hz, Me), 1.12 (d, 3H, J=6.8Hz, Me), 1.5-2.2 (m, 5H), 2.7-3.1 and 3.7-4.0 (m, each 1H, NCH_2), 3.19 (s, 3H, NMe), 6.59 (br t, 1H, NH); ^{13}C NMR δ 8.0 (q), 8.3 (q), 15.1 (q), 24.2 (t), 25.7 (t), 33.9 (q), 43.1

(d), 45.8 (t), 66.1 (s), 159.1 (s), 173.4 (s), 209.2 (s). Anal. Calcd for $C_{12}H_{20}N_2O_3$: C, 59.98; H, 8.39; N, 11.66. Found: C, 59.88; H, 8.46; N, 11.55.

1-Allyl-5,5-diethyl-6-hydroxy-3-methyldihydropyrimidine-2,4-dione (6f) could not be completely purified and did not give satisfactory analytical data; IR 3400, 1710, 1660cm^{-1}; characteristic signals ^{1}H NMR δ 5.2-5.4 (m, 2H, CH_2=), 5.7-6.1 (m, 1H, =CH-); ^{13}C NMR δ 27.8 (q), 49.4 (t), 49.6 (t), 81.7 (d), 119.1 (t), 133.3 (d), 152.5 (s), 173.5 (s).

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