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Nitration of 2-Substituted Pyrimidine-4,6-diones, Structure and Reactivity of 5,5-*gem*-Dinitropyrimidine-4,6-diones

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Nitration of some 2-substituted pyrimidine-4,6-diones in sulfuric acid was studied, which afforded previously unknown 5,5-*gem*-dinitropyrimidine-4,6-diones in high yields. The *gem*-dinitro products were easily attacked by nucleophiles with concomitant formation of *gem*-dinitroacetyl derivatives, which in turn could be further hydrolyzed to salts of dinitromethane and triureas.

Introduction

There are only a few examples of nitrations at saturated carbon atoms in aliphatic and heterocyclic molecules, leading to the formation of *gem*-dinitro- or trinitromethyl compounds.[1−5] Some substituted five-membered azolones have recently been shown to behave in the same way.[6−8] However, in those cases where *gem*-dinitration occurred in the heterocyclic ring it was accompanied by nitration either in the fused aromatic system or in the *exo*-cyclic substituent,[7] which made it difficult to differentiate the sequence of the nitration steps.

Trying to overcome these difficulties and to see if the presence of only carbonyl groups could promote *gem*-dinitration in nitrogen heterocyles we have studied the nitration of several pyrimidinones. Nitric acid in sulfuric acid was chosen as the reaction medium as this had previously been found to favor the formation of *gem*-dinitro compounds.[4−10]

2-Aminopyrimidine-4,6-dione (**1a**), barbituric acid (**1b**), and its *N*,*N*-dimethyl derivative (**1c**) were studied as compounds having only one reaction site, namely the 5-position in the ring, which might be susceptible to this type of nitration. The possibility of *N*-nitration was not excluded, but not taken into consideration, since the reversibility of this reaction[11] allows one to expect complete consumption of nitric acid in the irreversible formation of *C*-nitro compounds. The courses of the reactions were monitored by UV spectroscopy.

Discussion

It has long been known that nitration of barbituric acid (**1b**) in nitric acid at room temperature gives exclusive mononitration of the substrate in the 5-position.[12] The same results were obtained by us when compounds **1a**−**c** dissolved in concentrated sulfuric acid (85−95%) were treated with 1 equiv of nitric acid at room temperature. Quick and quantitative formation of 5-mononitro derivatives **2a**−**c** was observed. Excess of nitric acid in the nitrating mixture (1−1.5 mol per mol of **2a**−**c**) and a higher reaction temperature (30−60 °C) caused further nitration of these compounds. This was first detected by the appearance of a new absorption maximum (355−365 nm) in the UV spectra of the quenched samples in addition to the absorption maximum of the mononitrated products (320−330 nm).

It was not possible to study the kinetics of the second nitration step because of the strong overlap of the absorption curves from the mono- and dinitrated products. A rough estimation of reaction times could be obtained by following the smooth increase of the absorption at 360 nm. Maximum absorption was usually reached after a few hours whereupon it remained constant, thus indicating the formation of stable *C*-nitro compounds. Compound **1b** was completely converted to the *gem*-dinitrated product **3b** after 4 h at room temperature. 2-Aminopyrimidine-4,6-dione was found, not unexpectedly, to be more reactive, and consequently full

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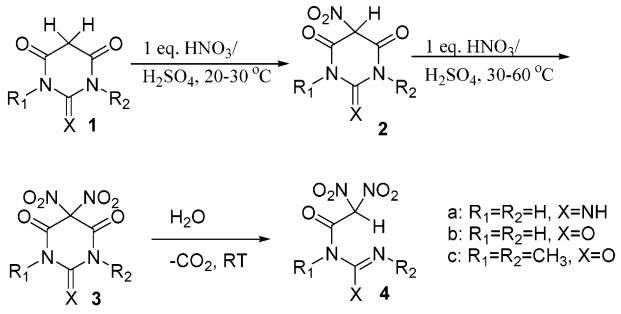
SCHEME 1



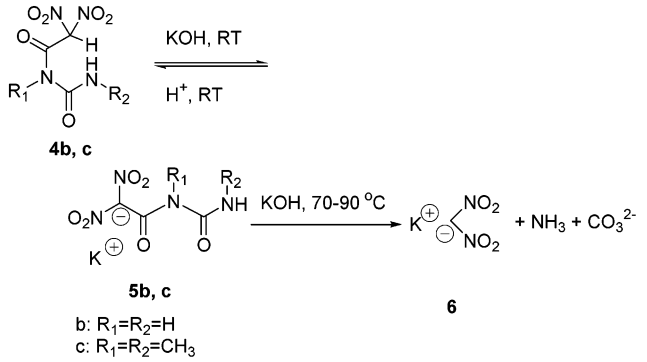
conversion to the corresponding dinitro derivative was observed after 2 h at ambient temperature. When the reaction medium was changed from sulfuric acid to oleum the rate of nitration decreased dramatically: nitration of **2b** in 101−105% sulfuric acid gave no *gem*-dinitro products after several days at the same reaction conditions. This is reminiscent of the observations made by Golod et al. while studying the nitration of nitroform.[13]

At higher concentrations (>5%) of the substrates **1b**,**c** in sulfuric acid the *gem*-dinitro products **3b**,**c** crystallized from the reaction media during the nitration. Both products reacted vigorously with water, forming derivatives of *gem*-dinitroacetylurea (**4b**,**c**), thus precluding aqueous workup of the reaction mixtures. Isolation of **3b**,**c** in pure form could only be achieved by repeated washing with trifluoroacetic acid (TFA) to remove all traces of sulfuric acid. Both compounds proved to be rather thermally stable (∼150 °C dec) and their structures as 5,5-*gem*-dinitro derivatives were confirmed by NMR studies and elemental analyses.

Dinitration of barbituric acid by nitrogen pentoxide in organic solvents had a long time ago been claimed by Runge,[14] who assigned the structure of the product as 1,5-dinitrobarbituric acid in analogy with other *N*-nitrated aliphatic amides in the series. Their assignment was exclusively based on the elemental analysis of the product in the form of a 1:1 complex with dioxane, despite the fact that the calculated figures for the suggested structure did not coincide with the experimental data; instead, the reported elemental analysis gives an excellent correlation with a 1:1 complex of *gem*-dinitroacetylurea (**4b**)and dioxane. Furthermore, in our hands, the described synthetic procedure gave exclusively a mixture of 5-nitro and 5,5-*gem*-dinitro barbituric acid. All these data imply that the authors were dealing with, in fact, *gem*-dinitrated barbituric acid. We were unable to isolate 2-amino-5,5-dinitropyrimidine-4,6-dione (**3a**) from the reaction media even at a very high substrate (**2a**) concentration (>20%), presumably due to the formation of a soluble salt as a result of protonation of the exocyclic amino function in the molecule. Neither did addition of TFA to the mixture help to induce its crystallization.

Formation of this product was postulated on the basis of the following results: the ensuing aqueous workup of the reaction mixtures produced by nitration of **1a** resulted, as in the case with solutions containing **3b**,**c**, in a vigorous reaction accompanied by evolution of carbon dioxide and precipitation of **4a**. This particular finding, summarized in Scheme 1, and compounds **3a**,**c** and **4a**,**c** were first presented by us in June 2000.[15] Half of a year later Boyle et al. described an analogous nitration of 2-amino-4,6-(3*H*,5*H*)-pyrimidinedione (**1a**) and 2-amino-6-chloro-4(3*H*)-pyrimidinone, as well as compound **4a**, without mentioning our original work.[16] Instead of mixed acids these authors used solutions of potassium nitrate in sulfuric acid, claiming that the latter system ensured a more easily controlled course of nitration and higher yields of *gem*-dinitrated products. Contrary to their observations we found that the use of mixed acids gave essentially the same results as the KNO_3 solutions. This is not too surprising since it is well-known that small amounts of both HNO_3 and KNO_3 are converted quantitatively in concentrated sulfuric acid to nitronium ions.[17]

SCHEME 2



Isolation of **3b**,**c** in pure form made it possible to study the properties and reactions of this type of compounds in more detail with **3b** as a typical representative. The presence of the strongly electronegative *gem*-dinitro group in the molecule rendered the adjacent carbonyl carbon atoms extremely susceptible to various nucleophiles, which was demonstrated by the easy hydrolytic ring cleavage during aqueous workup of the reaction mixtures (vide supra).

The nature of the products formed in these reactions was dependent on the reaction conditions used and the character of the nucleophile.

Compounds **3b**,**c** were demonstrated to dissolve readily in cold water forming acidic solutions, from which on standing carbon dioxide evolved resulting in the precipitation of *gem*-dinitroacetylureas **4b** and **4c**. These compounds are strong acids forming rather insoluble salts on careful neutralization of their aqueous solutions (**5b**,**c**) (Scheme 2). Treating **5b**,**c** with potassium hydroxide under more vigorous reaction conditions led to the formation of potassium dinitromethanide (**6**) in high yield.

Weak nucleophiles such as alcohols react smoothly with **3b** at ambient temperature forming derivatives of the urethane (**9**), thus confirming that the reaction site for the initial nucleophilic attack is the 4(6)-carbonyl

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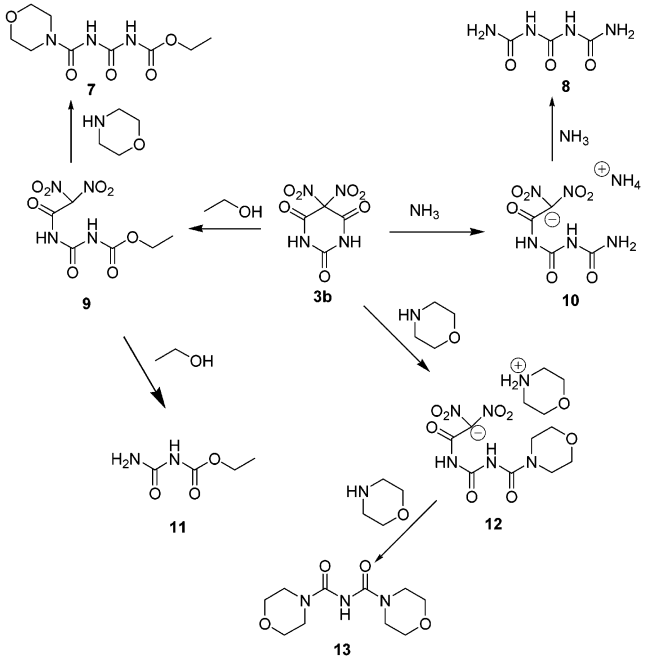
SCHEME 3



carbon. Thiols proved to be too weak nucleophiles and did not react with **3b**, instead ring opening with water was observed. Certain nucleophiles such as amines and ammonia reacted violently with **3b** and formed rather complex mixtures of products, so that low temperature and high dilution of reagents had to be used to achieve a controlled course of the reaction. Under these conditions pure products of the type **10** and **12** were isolated in relatively high yields. The results are summarized in Scheme 3.

It was found that these compounds were also liable to nucleophilic attacks, though in this case more vigorous reaction conditions were necessary (Scheme 3). In most cases the reaction site was again the carbonyl carbon adjacent to the *gem*-dinitro group with the latter acting as a leaving group. The reaction products varied depending on the nature of the nucleophile used: reactions with amines lead to formation of symmetrical (**8**) or unsymmetrical triureas (**7**) and probably salts of dinitromethane (as was indicated by UV spectroscopy of the mother liquor). There was only one example of a nucleophilic attack at the urea carbon. In the reaction of **12** with morpholine **13** was formed; however, the reaction of **9** with ethanol gave **11**.

Similar reactions of 5,5-disubstituted barbituric acids were observed by Ziegler and Kappe while investigating the properties of 5-chloro-5-nitrobarbituric acid (**14**). Thus treating **14** with water led to evolution of carbon dioxide and precipitation of chloronitroacetyl urea (**15**).[18] Reaction with other nucleophiles also resembles the behavior of **3b**, where the treatment of **14** with morpholine led to isolation of the morpholinium salt of 1-(2-chloro-2-nitroacetyl)-3-(morpholino-4-carbonyl)urea (**16**). It was of interest to elucidate the structural configuration of the rather unusual group of dinitroacetylureas **4a**−**c**. As an example, the potassium salt of 2,2-dinitroacetylurea (**5b**),

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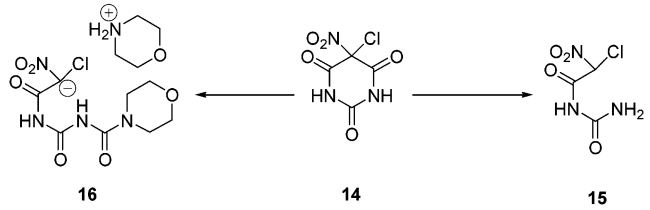
SCHEME 4



which easily forms suitable crystals, was investigated by single-crystal *X*-ray diffraction methods.

The unit cell consists of two molecules, **a** and **b**, with slightly different out of plane angles of one of the two nitro groups present in each molecule as can be seen in Figure 1. The entire unit cell, both **a** and **b**, is planar and only one of the *gem*-dinitro groups in each molecule is out of the plane. In molecule **a** this nitro group is bent downward and in molecule **b** it is bent upward (Figure 1). The geometries of the nitro groups are as expected, having one shorter and one longer nitrogen−oxygen bond, with bond distances varying between 1.23(1) and 1.26(1) Å.

The following bond distances are obtained for the nitrogen, oxygen, and carbon atoms in the main chain of the two molecules excluding the nitro group oxygen atoms: N(4a)-C(3a)-O(4a)- -N(3a)-C(2a)-O(2a)- -C(1a)-N(1a)- -N(2a) 1.30, 1.23, 1.41, 1.38, 1.23, 1.48, 1.39, and 1.41 Å with esd's of 0.01 Å and N(4b)-C(3b)-O(4b)- -N(3b)-C(2b)-O(2b)- -C(1b)-N(1b)- -N(2b) 1.34, 1.23, 1.40, 1.37, 1.23, 1.46, 1.40, and 1.41 Å with esd's of 0.01 Å, respectively. The bond angles around the carbon atoms C(1)−C(3) all lie in the interval of 117−122°. The bond distances and angles for the two molecules **a** and **b** clearly indicate sp^2-hybridization of the carbon. The planar geometry of the *gem*-dinitroacetylurea ion is stabilized by strong intramolecular hydrogen bonding. Two of the three hydrogen atoms in each molecule are participating in strong intramolecular hydrogen bonding with the following donor−acceptor distances O(21a)−N(3a) 2.64(1) Å, N(4a)−O(2a) 2.67(1) Å, O(21b)−N(3b) 2.67(1) Å, N(4b)−O(2b) 2.67(1) Å. The two hydrogen bonds are both part of a six-membered intramolecular ring conformation, stabilizing the planar configuration.

Additional evidence for the presence of hydrogen bonding in the molecule came from the analyses of the ^{1}H NMR spectrum of the potassium salt of **4b**. Normally one would expect two peaks in the ^{1}H NMR spectrum, instead three peaks were observed at room temperature corresponding to the NH and NH_2 groups. This made us believe that one of the hydrogen atoms in the NH_2 group is participating in hydrogen bonding thus leading to splitting of the NH_2 peak. To verify this hypothesis dynamic ^{1}H NMR experiments were performed on the salt with DMSO-d_6 as solvent.

Variable-temperature ^{1}H NMR measurements were performed in the range from +25 to +75 °C. At each temperature the sample was stabilized for a minimum of 10 min.

A relatively high coalescence temperature (65 °C) was observed for substance **6b** when the NH-doublet at 7.5 ppm merged into a singlet at 7.0 ppm and a $\Delta\nu$ = 145 Hz was observed at room temperature (298 K) (Figure 2). From these figures the activation energy for

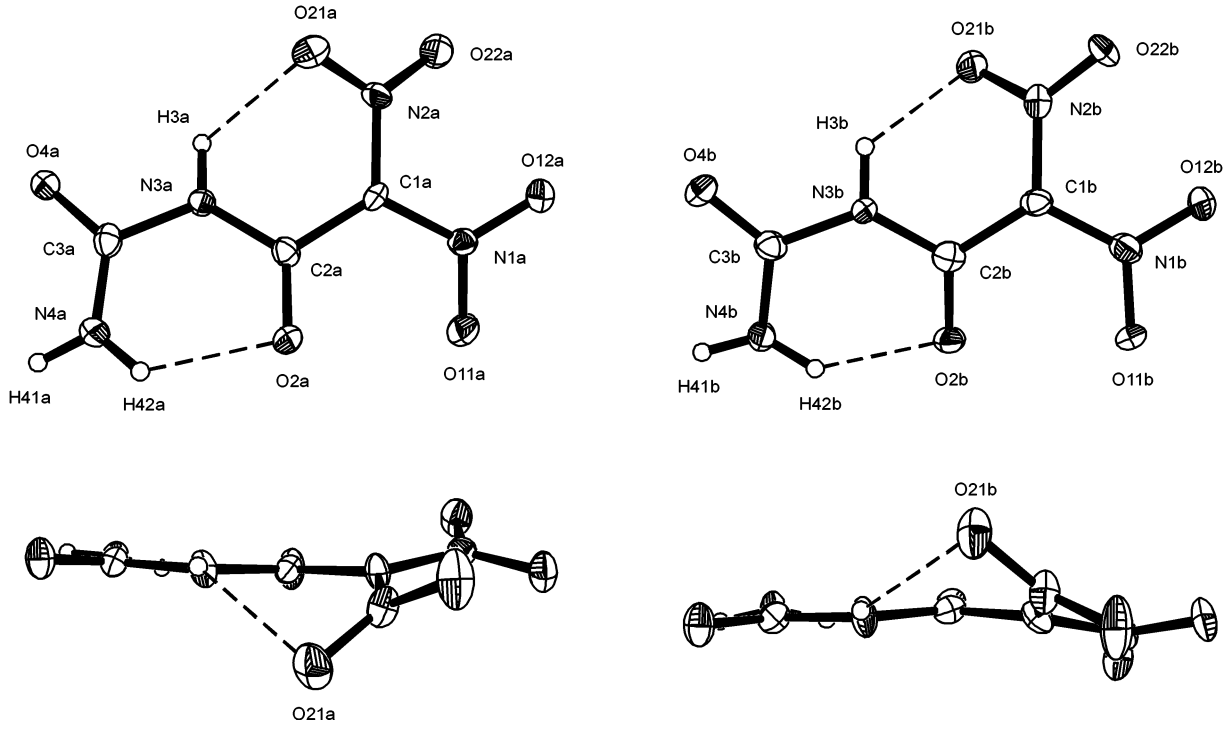


FIGURE 1. The molecular conformation and atom labeling of the *gem*-dinitroacetylurea ion. Molecule **a** on the left and **b** on the right. The lower figure illustrates the planar geometry of the molecule and the different angle of one of the two nitro groups.

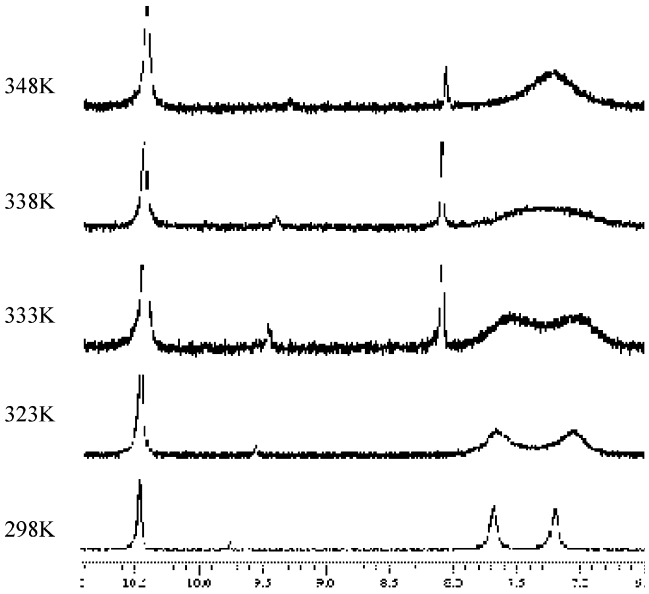


FIGURE 2. Partial variable-temperature 300-MHz ^{1}H NMR spectra recorded in DMSO-d_6.

rotation ($\Delta G^{\ddagger}$) was calculated according to the Eyring equation:[25]

$$\Delta G^{\ddagger}_{T_c} = 4.58 T_c(10.32 + \log T_c/k_c) \text{ cal/mol}$$

where $k_c = \pi\Delta\nu/\sqrt{2}$ and $T_c = 338$ K. $\Delta G^{\ddagger}$ was found to be equal to 16.0 kcal/mol, thus indicating the existence of strong hydrogen bonding and hindered rotation around C(3) and N(4). At elevated temperatures an additional peak at ca. 8.1 ppm appears, which probably originates from the anion of dinitromethane (**6**)[16,19] produced by partial hydrolysis of the substance.

Summary and Conclusions

gem-Dinitration in the heterocyclic ring of the pyrimidinone series (barbituric acid, 1,3-dimethylbarbituric acid, and 2-amino-4,6-dihydroxypyrimidine) was discovered. The *gem*-dinitro compounds formed were easily hydrolyzed to derivatives of *gem*-dinitroacetylurea and *gem*-dinitroacetylguanidine, which could be further hydrolyzed to dinitromethane salts. Ring opening of *gem*-dinitro pyrimidinones with nucleophiles gave new *gem*-dinitroacetyl derivatives, while more forcing conditions and strong nucleophiles gave symmetric or asymmetric triurea compounds as well as salts of dinitromethane. Hydrolysis of 5,5-dinitrobarbituric acid provides a new, efficient, and safe method for the preparation of dinitromethane in comparison with other known methods.[20−22]

Experimental Section

NMR spectra were obtained on a Bruker Avance 400 or a JEOL Eclipse+ 500. Infrared spectra were recorded with a Perkin-Elmer 1600 FTIR. Melting points and decomposition temperatures were recorded with a Mettler DSC 30. Elemental analyses were carried out by H Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

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Caution: The *gem*-dinitrocompounds described in this paper are powerful and sensitive explosives and should be handled with appropriate precautions. Employ all standard energetic materials safety procedures in experiments involving such substances. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 143142. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. (fax: +44(0)-1223−336033 or e-mail: deposit@ccdc.cam.ac.uk).

5,5-Dinitrobarbituric Acid (3b). To a mixture of barbituric acid (**1b**) (12.8 g, 0.1 mol) dissolved in 95% sulfuric acid (60 mL) was added fuming nitric acid (10 mL, 0.24 mol) while the temperature was kept below 25 °C. The reaction mixture was then heated to 45 °C for 4 h. The resulting precipitate was filtered, washed with TFA, and dried, yielding 5,5-dinitrobarbituric acid (**3b**) as a hemihydrate (21.3 g, 0.094 mol, 94%), 150 °C dec; IR (KBr) 3252(NH), 1745 (C═O), 1611 (C═O), 1580 $C(NO_2)_2$, 1378 $C(NO_2)_2$; ^{1}H NMR (DMSO-d_6) δ 11.03 br; ^{13}C NMR (DMSO-d_6) δ 113.5, 149.0, 155.1. Anal. Calcd for $C_4H_2N_4O_7 \cdot {}^1/_2H_2O$: C, 21.16; H, 1.33; N, 24.67. Found: C, 21.11; H, 1.23; N, 24.89.

1,3-Dimethyl-5,5-dinitropyrimidine-2,4,6-trione (3c). *N*,*N*′-Dimethyldinitrobarbituric acid (**1c**) (3.9 g, 0.025 mol) was added to sulfuric acid (78 mL, 95%), and nitric acid (2.3 mL, 0.055 mol) was added dropwise at 30 °C during 30 min. The temperature was raised to 40 °C for 4.5 h. A white precipitate was formed after 30 min. After standing at ambient temperature for 3 h the precipitate was collected and washed with TFA, yielding 1,3-dimethyl-5,5-dinitropyrimidine-2,4,6-trione (**3c**) (4.8 g, 0.0195 mol, 78%); IR (KBr) 1715 (C═O), 1597 $C(NO_2)_2$, 1366 $C(NO_2)_2$; ^{1}H NMR (DMSO-d_6) δ 3.28; ^{13}C NMR (DMSO-d_6) δ 154.14, 149.13, 107.73, 31.10; mp 178 °C. Anal. Calcd for $C_6H_6N_4O_7$: C, 29.28; H, 2.46; N, 22.76. Found: C, 29.38; H, 2.51; N, 22.59.

***gem*-Dinitroacetylurea (4b).** Dinitrobarbituric acid (**3b**) (7.2 g, 0.032 mol) was dissolved at 10 °C in water (10 mL) and kept at this temperature for 2 h; during this period gas evolution was observed, which resulted in the precipitation of a yellow solid. The solid was filtered and dried at 40 °C with a color change from yellow to white to give **4b** (5.5 g, 0.017 mol, 53%); 130 °C dec; IR (KBr) 3501 ($CONH_2$), 3045 ($CONH_2$), 1780 ($CONH_2$), 1719 ($CONH_2$), 1595 $C(NO_2)_2$), 1356 $C(NO_2)_2$); ^{1}H NMR (CD_3NO_2) δ 9.4 (br s, 1H), 7.64 (br s, 1H), 5.94 (br s, 1H). Anal. Calcd for $C_3H_4N_4O_6$: C, 18.75; H 2.08; N, 29.17. Found: C, 18.78; H, 2.26; N, 29.14. It was not possible to obtain a carbon-13 NMR of *gem*-dinitroacetylurea (**4b**) due to low stability in solution.

Potassium *gem*-Dinitroacetylurea (5b). *gem*-Dinitroacetylurea (**4b**) (10 g, 0.052 mol) dissolved in water (50 mL) was added dropwise to a solution of KOH (2.7 g, 0.05mol) in 50 mL of water while keeping the temperature at 10 °C. A yellow precipitate was immediately formed, which was filtered and dried. Yield 8.2 g (0.027 mol, 77%) of potassium *gem*-dinitroacetylurea (**5b**); 160 °C dec; IR (KBr) 3418 ($CONH_2$), 3335 ($CONH_2$), 1728 ($CONH_2$), 1635 ($CONH_2$), 1580 $C(NO_2)_2$), 1398 $C(NO_2)_2$); ^{1}H NMR (DMSO-d_6) δ 10.44, 7.66, 7.21; ^{13}C NMR (DMSO-d_6) δ 159.15, 154.90, 134.99. Anal. Calcd for $C_3H_3N_4O_6K$: C, 15.65; H, 1.31; N, 24.34. Found: C, 15.46; H, 1.28; N, 24.22.

One-Pot Preparation of Potassium Salt of (2,2-Dinitroacetyl)urea (4b) from *gem*-Dinitrobarbituric Acid (3b). 5,5-Dinitrobarbituric acid (**3b**) (5 g, 0.022 mol) was added to water (10 mL) at 10 °C and a solution of potassium hydroxide (1.3 g, 0.023 mol) in water (5 mL) was added. Gas evolution was observed. The temperature was raised to 25 °C for 30 min. A yellow precipitate was formed. The precipitate was collected and dried to yield the potassium salt of (2,2-dinitroacetyl)urea (**4b**) as yellow crystals (3.2 g, 0.014 mol, 63%).

Potassium Salt of *N*,*N*-Dimethyl-*gem*-dinitroacetylurea (5c). *N*,*N*-Dimethyl-*gem*-dinitrobarbituric acid (**3c**) (0.25 g, 0.001 mol) was added to a solution of potassium carbonate (0.002 mol) in water (30 mL) and a pale yellow precipitate was formed (0.19 g, 0.75 mmol, 75%). IR (KBr) 3428, 3024, 1687 (C═O), 1574 $C(NO_2)_2$), 1334 $C(NO_2)_2$); ^{1}H NMR (DMSO-d_6) δ 8.73 (q, 1H, J = 4.02), 3.38 (s, 3H), 2.76 (d, 3H, 4.02); ^{13}C NMR (DMSO-d_6) δ 165.06, 155.67, 131.77, 31.73, 27.75; 190 °C dec, Anal. Calcd for $C_5H_6N_4O_6K$: C, 23.26; H, 2.73; N, 21.70. Found: C, 23.37; H, 2.80; N, 21.64.

Potassium Dinitromethane (6). Potassium *gem*-dinitroacetylurea (**5b**) (10 g, 0.052 mol) was added to the solution of KOH (12 g, 0.21 mol) in water (100 mL); the resulting mixture was kept at 80 °C for 2 h and then cooled to room temperature. The precipitate of potassium dinitromethane was filtered, washed with 10−15 mL of cold water, and dried to give 6.2 g (0.044 mol, 85%) of pure potassium dinitromethane (**6**), which was identified by its decomposition temperature of 220 °C[20] and UV spectroscopy (λ_{max} = 363 nm and ϵ = 20 800);[16,19] ^{1}H NMR (DMSO-d_6) δ 8.16; ^{13}C NMR (DMSO-d_6) δ 123.66.

***gem*-Dinitroacetylguanidin (4a).** 2-Aminopyrimidine-4,6-dione (**1a**) (3.8 g, 0.018 mol) dissolved in concentrated sulfuric acid (40 mL) was nitrated under conditions analogous to those for **3b**. After 2 h the reaction mixture was cooled to room temperature and poured into cold water (200 mL); the dilution was accompanied by evolution of carbon dioxide and precipitation of a yellow solid, **4a** (5.0 g, 0.016 mol, 88%); 150 °C dec; IR (KBr) 3412 ($CONH_2$), 1685 ($CONH_2$), 1672 ($CONH_2$), 1572 $C(NO_2)_2$), 1371 $C(NO_2)_2$); ^{1}H NMR (DMSO-d_6) δ 11.4 (br s, 1H), 8.8 (br s, 2H), 8.11 (br s, 2H); ^{13}C NMR (DMSO-d_6) δ 157.55, 155.75, 135.34. Anal. Calcd for $C_3H_5N_5O_5$: C, 18.85; H, 2.62; N, 36.65. Found: C, 19.01; H, 2.60; N, 36.57.

Ammonium Salt of (2,2-Dinitroacetyl)biuret (10) and Ureoidocarbonylurea (8). 5,5-Dinitrobarbituric acid (**3b**) (2 g, 0.009 mol) was added to ammonia (40 mL, 25%) at 5−10 °C. A yellow precipitate was formed. A sample was collected and dried, yielding yellow crystals of the ammonium salt of (2,2-dinitroacetyl)biuret (**10**) as a dihydrate; 94 °C dec; IR (KBr) 3447 (NH_4^+), 1742 ($CONH_2$), 1510 $C(NO_2)_2$), 1395 $C(NO_2)_2$); ^{1}H NMR (DMSO-d_6) δ 11.04 (s, 1H), 10.06 (s, 1H), 7.35 (s, 2H), 7. 7 (s, 4H); ^{13}C NMR (DMSO-d_6) δ 158.88, 153.79, 152.37, 134.54. Anal. Calcd for $C_4H_8N_6O_7 \cdot 2H_2O$: C, 16.67; H, 4.16; N, 29.16. Found: C, 16.37; H, 4.16; N, 29.16. The reaction mixture was refluxed for 20 min and a white precipitate was formed. The precipitate was collected, washed with ethanol, and dried, yielding ureoidocarbonylurea (**8**) (0.32 g, 0.002 mol, 24%). Elemental analysis and spectroscopic data were in all respects identical with data given in the literature.[23]

Morpholine Salt of 1-(2,2-Dinitroacetyl)-3-(morpholine-4-carbonyl)urea Complexed with 1 equiv of Morpholine (12). 5,5-Dinitrobarbituric acid (**3b**) (1 g, 0.0045 mol) was added to morpholine (30 mL) at 0−10 °C. After addition the reaction mixture was heated to 30 °C for 10 min. Cooled diisopropyl ether (30 mL) was added and a white precipitate was formed. The precipitate was collected, washed with ethanol, and dried, yielding the morpholine salt of 1-(2,2-Dinitroacetyl)-3-(morpholine-4-carbonyl)urea (**12**) as a complex with one molecule of morpholine (2.1 g, 0.0043 mol, 97%); 150 °C dec; IR (KBr) 3412 ($R_2NH_2^+$), 1737 (C═O), 1524 $C(NO_2)_2$), 1398 $C(NO_2)_2$); ^{1}H NMR (DMSO-d_6) δ 7.29 (br s, 4H, NH), 3.65 (t, 8H, CH_2, J = 5.0 Hz), 3.58 (t, 4H, CH_2, J = 5.0 Hz), 3.40 (t, 4H, J = 5.0 Hz) 2.93 (t, 8H, CH_2, J = 5.0 Hz); ^{13}C NMR (DMSO-d_6) δ 157.53, 151.82, 149.46, 133.92, 65.72, 64.80, 44.09. Anal. Calcd for $C_{16}H_{29}N_5O_{10}$: C, 40.08; H, 6.05; N, 20.45. Found: C, 39.64; H, 6.08; N, 20.30.

1-(2,2-Dinitroacetyl)-3-(carbonyl ethyl ester)urea (9). 5,5-Dinitrobarbituric acid (**3b**) (2 g, 0.011 mol) was added to ethanol (10 mL). The mixture was heated to 79 °C for 30 min resulting in a yellow solution, which was concentrated to 5 mL; hexane (20 mL) was added to the solution and a yellow precipitate was formed. The precipitate was collected and dried, yielding 1-(2,2-dinitroacetyl)-3-(carbonyl ethyl ester)urea

(23) Haworth, R. C.; Mann, F. G. *J. Chem. Soc.* **1943**, 603−606.

(**9**) (1.3 g, 0,005 mol, 44%); 120 °C dec; IR (KBr) 3368 ($CONH_2R$), 1702 (C═O), 1657 (C═O)1575 ($C(NO_2)_2$), 1238 ($C(NO_2)_2$); ^{1}H NMR (DMSO-d_6) δ 11.41 (s, 1H), 11.64 (s, 1H), 10.30 (br s, 1H), 4.14 (q, 2H, CH_2, J = 7.1 Hz), 1.22 (t, 3H, CH_3, J = 7.1 Hz); ^{13}C NMR (DMSO-d_6) δ 157.48, 155.27, 149.55, 134.80, 62.72, 14.82. Anal. Calcd for $C_6H_8N_4O_8$: C, 27.28; H, 3.05; N, 48.46. Found: C, 27.64; H, 3.15; N, 20.96.

5,5-Dinitrobarbituric acid (**3b**) (4 g, 0.0183mol) was added to ethanol (15 mL) and the mixture was refluxed for 40 min. The yellow precipitate formed was filtered, washed with petroleum ether, and dried, yielding 1-(2,2-dinitroacetyl)-3-(carbonyl ethyl ester)urea (**9**) (4.12 g, 0.0156 mol, 85%).

Ethyl(aminocarbonyl)carbamat from 5,5-Dinitrobarbituric Acid (11). 5,5-Dinitrobarbituric acid (**3b**) (2 g, 0.011 mol) was added to ethanol (15 mL) at ambient temperature. After 48 h a white precipitate was collected and characterized as ethyl(aminocarbonyl)carbamate.[24]

Morpholine Salt of 1-(2-Chloro-2-nitroacetyl)-3-(morpholino-4-carbonyl)urea (16). 5-Chloro-5-nitrobarbituric acid (**14**) (2 g, 0.0097 mol) was added to morpholine with cooling. The reaction mixture was refluxed for 15 min, yielding pale red precipitate; dioxane was added (10 mL) and the precipitate was collected. Recrystalization from dioxane (40 mL) gave 1-(2-chloro-2-nitroacetyl)-3-(morpholine-4-carbonyl)-urea (**16**) as a morpholine salt (2.1 g, 0.0055 mol, 57%); 170 °C dec; IR (KBr) 3062 ($R_2NH_2^+$), 1742 (C═O_2), 1636 (C═O); ^{1}H NMR (DMSO-d_6) δ 12.51 (s, 1H, NH), 11.11 (s, 1H, NH), 8.62 (br s, 2H, NH_2), 3.75 (t, 4H, CH_2, J = 5.0 Hz), 3.60 (t, 4H, CH_2, J = 5.0 Hz), 3.38 (t, 4H, CH_2, J = 5.0 Hz), 3.10 (t, 4H, CH_2, J = 5.0 Hz); ^{13}C NMR (DMSO-d_6) δ 160.27, 150.87, 149.38, 108.85, 65.73, 65.37, 42.98. Anal. Calcd for $C_{12}H_{20}ClN_5O_7$: C, 37.75; H, 5.28; N, 18.34. Found: C, 37.45; H, 5.25; N, 17.54.

1-(Morpholino-4-carbonyl)-3-(carbonyl ethyl ester)-urea (7). 1-(2,2-Dinitroacetyl)-3-(carbonyl ethyl ester)urea (**9**) (2 g, 0.0076 mol) was added to a solution of morpholine (1.3 mL, 0.015 mol) in dioxane (11 mL). The reaction mixture was refluxed for 30 min and a pale red precipitate was formed. Recrystallization from dioxane (20 mL) and drying gave 1-(morpholin-4-carbonyl)-3-(carbonyl ethyl ester)urea (**7**) (0.5 g, 0.0017 mol, 23%) as white crystals; mp 180 °C; IR (KBr) 3262 ($CONH_2R$), 1800 (CO_2R), 1694 (C═O), 1657 (C═O); ^{1}H NMR (DMSO-d_6) δ 10.96 (s, 1H, NH), 9.78 (s, 1H, NH), 4.12 (q, 2H, CH_2, J = 7.1 Hz), 3.57 (t, 4H, CH_2, J = 4.7 Hz), 3.41 (t, 4H, J = 4.7 Hz), 1.21 (t, 3H, CH_3, J = 7.1 Hz); ^{13}C NMR (DMSO-d_6) δ 153.17, 151.52, 149.36, 65.66, 61.38, 44.15, 14.08. Anal. Calcd for $C_9H_{15}N_3O_5$: C, 44.08; H, 6.17; N, 17.13. Found: C, 44.15; H, 5.80; N, 17.15.

Bis(morpholino-4-carbonyl)amide (13). 5,5-Dinitrobarbituric acid (3 g, 0.0135 mol) was added to morpholin (16.5 mL) at 0−10 °C. The reaction mixture was heated to reflux for 1 h. On cooling an orange precipitate was formed. The precipitate was collected and washed with *n*-heptane and dioxane; recrystallization from dioxane (40 mL) gave bis-(morpholin-4-carbonyl)amide (**13**) (1 g, 0.0046 mol, 34%) as white needles; mp 180 °C; IR (KBr) 2975 (CH_2), 1685 (C═O), 1651 (C═O) 1248 (C═O); ^{1}H NMR (DMSO-d_6) δ 8.60 (s, 1H, NH), 3.54 (t, 8H, CH_2, J = 5.0 Hz), 3.32 (t, 8H, CH_2, J = 5.0 Hz); ^{13}C NMR (DMSO-d_6) δ 154.19, 66.91, 44.56. Anal. Calcd for $C_{10}H_{17}N_3O_3$: C, 49.37; H, 7.04; N, 17.27. Found: C, 49.10; H, 7.81; N, 17.18.

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