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Study on Reactions of 2-(Dinitromethylene)-4,5-imidazolidinedione

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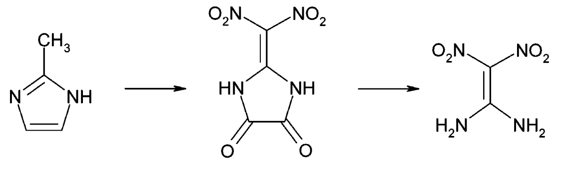
Some new reactions of 2-(dinitromethylene)-4,5-imidazolidinedione (**1**) with water, alcohols, carboxylic acids, and alkalis were discovered. By reaction of **1** with carboxylic acids, large particle size 1,1-diamino-2,2-dinitroethylene (**2**) was prepared. By reaction of **1** with methanol, the methanol adduct (**4)** was synthesized and characterized. By reaction of **1** with water, the synthetic pathway of 2-methylimidazole to **2** could be achieved in a continuous process. By reaction of **1** with KOH, **2** and potassium dinitromethane (**6**) could be formed at different temperature, respectively. Compounds **1** and **4** decomposed into parabanic acid (**5)**, losing nitrogen oxides and carbon oxides. Some explosive properties of **1** were studied. The mechanisms of synthesis of **1**, **2**, and **5** are discussed.

1. Introduction

2-(Dinitromethylene)-4,5-imidazolidinedione (**1**) was reported in 1998 for the first time.[1] It is an important intermediate which can be aminated to form 1,1-diamino-2,2-dinitroethylene (**2**) by aqueous ammonia (see Scheme 1). Compound **2** is also named as FOX-7, with high performance and low sensitivity, and is known to be a new energetic material with promising properties as an attractive ingredient for application in high explosive formulations.[2] In recent years, many properties of FOX-7 have been studied.[3−8]

But except for this reaction, no more new reactions involving with **1** have been reported up to now, so the chemical properties of **1** are not investigated sufficiently. Our experiments have confirmed that **1** has many new reaction characters. In the structure of **1**, the amide bonds are reactive and easy to break, while the *gem*-dinitro is unstable and also easy to decompose. In addition, **1** is an explosive and can explode in certain conditions to produce a great deal of gas products, so we have expected that **1** can process three different reactions: ring cleavage, losing nitrogen oxides, and explosive decomposition. These have indeed proved to be the case.

SCHEME 1



1 **2**

Through experiments we have synthesized the methanol adduct of **1** and have mastered the preparation method of **2** with large particles, which can be used in the formulation directly and do not need recrystallization.

2. Results and Discussion

2.1. Ring Cleavage. The carbonylation in molecule **1** links with amino directly and is strongly polarized. The highly electronegative oxygen leaves the carbon atom a partial positive charge. Therefore, it is reasonable to expect nucleophilic reagents or nucleophiles to attack the carbon atom of the carbonylation.[9] The reaction of **1** with nucleophiles such as KOH, CH_3OH, H_2O, and HCOOH can be accounted for on this basis.

Attempts to obtain product **3 (**see Scheme 2) failed. The possible reason was that **3** was unstable and easily attacked by the second nucleophile. The experimental results indicated that the two carbonylations could be replaced, and then **2** and the corresponding oxalic derivatives were produced (see Scheme 3).

2.1.1. Reaction of 1 with Methanol. Compound **1** was treated with dilute hydrogen chloride to form a

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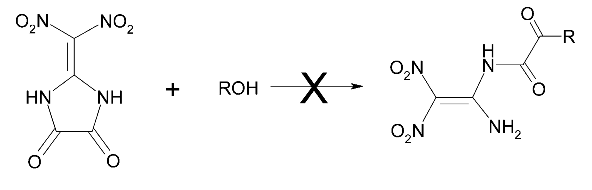
10.1021/jo030395f CCC: $27.50

SCHEME 2



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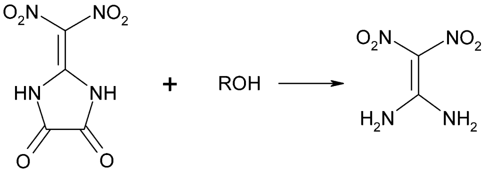
SCHEME 3



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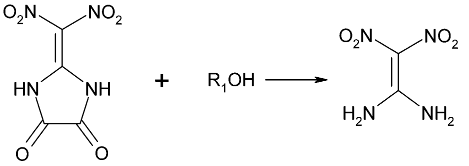

SCHEME 5

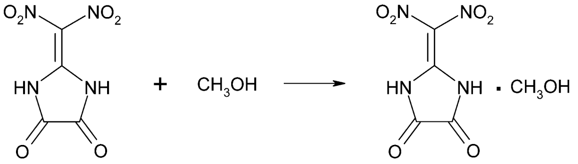

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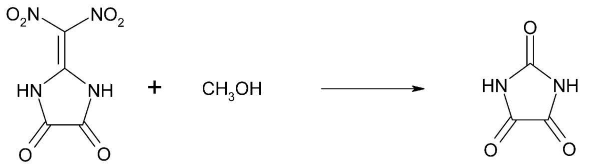
TABLE 1. Effect of Temperature on Yield of the Products[a]

T (°C)	0	20	40	60
yield of the adduct (%)	12.8	98.0	95.1	21.0
yield of FOX-7 (%)	0	0	0	74.3
yield of parabanic acid (%)	14.9	0	3.3	2.1

[a] Methanol (200 mL), 2-(dinitromethylene)-4,5-imidazolidinedione (0.01 mol), reaction 30 min, Fe and dilute hydrogen chloride (catalytic amount).

SCHEME 6



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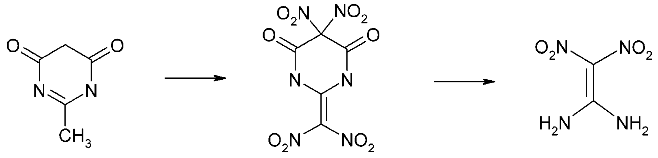
SCHEME 7



2

mixture at >50 °C. When methanol was added, the white solid dissolved immediately to form a yellow solution, and in a few seconds bright yellow crystals precipitated. Spectral analysis proved the product was **2** (see Scheme 4).

When **1** was treated with methanol at ambient temperature, yellow needle crystals **4** (see Scheme 5) were formed. Spectral analysis proved **4** was a methanol adduct of **1**. Compound **4**, now reported for the first time, is the first adduct of **1**. It cannot be dissolved in common organic solvents and water, is found to be more thermally stable than **1**, and can exist stably in the air for a long time. The thermogravimetry (TG) spectrum shows at least three steps. This gives an indication that a three-step process characterizes the initial decomposition of **4**. The differential scanning calorimetry (DSC) spectrum of **4** shows a complex structure with one endothermal peak (131 °C) and three exothermal peaks (135, 175, 231 °C). More experiments have confirmed that under certain conditions **1** could also react with other alcohols, for example, ethanol, but the product was **2**, not adducts. The details of physical properties and the single-crystal X-ray diffraction studies of **4** are being carried out.

There were many factors affecting the synthesis of **4**, and temperature was one of the most important factors. The effect of temperature on yield of the products was given in Table 1. Experiments indicated that high yield of **4** was achieved in the range of 10−40 °C (98.0% optimum at 20 °C). Temperatures below 10 °C gave a low yield of **4**, and parabanic acid (**5**) was the major product formed (14.9% optimum at 0 °C, see Scheme 6). While a higher reaction temperature (above 50 °C) caused ring cleavage of **1**, **2** was the major product (74.3% optimum at 60 °C).

There were three routes in the reaction of **1** with methanol, so three different products (**2**, **4**, and **5**) were formed. Generally, more energy was needed in the reaction of ring cleavage, so Scheme 4 proceeded easily when the temperature was high (above 50 °C), while little energy was needed in the self-decomposition of **1**, so Scheme 6 proceeded easily when the temperature was low (below 0 °C). Forming hydrogen bonds was essential for producing the methanol adduct, which needed appropriate energy, so Scheme 5 proceeded easily at the proper temperature (10−40 °C).

2.1.2. Reaction of 1 with Water.

Recently, it has been reported that FOX-7 was synthesized in a plant on a multikilogram scale in Sweden[4] and the route used was Scheme 7.[10]

Dinitromethane was formed as a byproduct, which is very unstable and explosive, so the safety of this process is low and there has been a continuous interest in adapting Scheme 1 as a possible production pathway. At present, the cost of Scheme 1 is very high due to the low overall yield of FOX-7 (about 13%). We have investigated Scheme 1 recently and found two main disadvantages:[11] first, **1** needs to be separated and purified, but pure **1** is sensitive to explosive the process of its separation and purification is dangerous. Second, trifluoroacetic acid is used to purify **1**, but it is very expensive, impure, and

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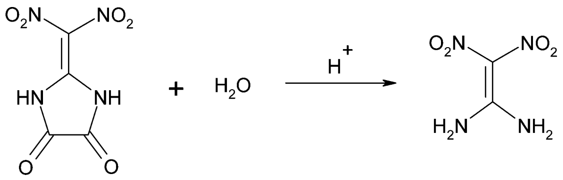
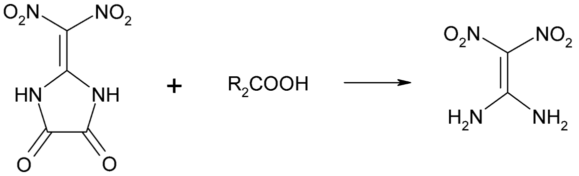
SCHEME 8



SCHEME 9



hard to reclaim. By reaction of **1** with water these disadvantages could be removed.

Compound **1** was treated with dilute hydrogen chloride or sulfuric acid to form a mixture at 25 °C. When the mixture was added to water dropwise, the white solid dissolved immediately to form a straw yellow solution and in a few seconds bright yellow crystals precipitated (81.1% yield under optimal conditions); spectral analysis proved the product was **2** (see Scheme 8).

Water is cheaper than aqueous ammonia, so if this technique is used for the scale-up of **2**, the synthetic pathway of 2-methylimidazole to FOX-7 (see Scheme 1) could be achieved in a continuous process. This improvement makes it possible that the large-scale production of FOX-7 can proceed at low cost.

2.1.3. Reaction of 1 with Carboxylic Acid. We have expected that **1** can be attacked by carboxylic acids and converted to **2** and corresponding oxalic anhydrides. This expectation has been shown to be correct (see Scheme 9).

In our experiment, liquid carboxylic acids such as formic acid, acetic acid, propanoic acid, *n*-butanoic acid, and *n*-pentanoic acid reacted with **1** to form corresponding oxalic anhydrides. The major byproduct formed was parabanic acid. This kind of reaction has offered a new method to prepare oxalic anhydrides, but it was difficult to isolate these compounds. In addition, the crystallizing rate of **2** was slower while the particle size of the crystal was larger.

The particle size of FOX-7 produced in Sweden was much too small to be used directly,[4] for example, in the formulation research. Therefore, the raw product was recrystallized in a mixture of *N*-methylpyrrolidone and water. Through reaction of **1** with carboxylic acids, we have mastered the preparation of large particle size **2** (approximately 20−1000 μm), which was obtained directly and did not need recrystallization. In these reactions, the yield of **2** was very high while the yield of byproduct parabanic acid was very low (Table 2). The style of crystal was different from that recrystallized by *N*-methylpyrrolidone and water. Scanning electron microscope (SEM) photographs are displayed in Figure 1.

2.1.4. Reaction of 1 with KOH. If **1** was dissolved in dilute aqueous KOH at ambient temperature, FOX-7 was formed by ring cleavage. However, it was shown that under more vigorous reaction conditions (T > 60 °C) **1** dissolved in concentrated aqueous KOH and was easily hydrolyzed to potassium dinitromethane (**6**) in a 65.3% yield (see Scheme 10). Melting point and UV analysis of the product were consistent with those reported previously.[12,13]

TABLE 2. Yield of the Product Synthesized by the Reaction of 1 with Carboxylic Acid[a]

carboxylic acid	yield of **2** (%)	yield of **5** (%)
formic acid	94.6	2.6
acetic acid	95.8	2.5
propanoic acid	95.8	2.7
n-butanoic acid	96.6	1.8
n-pentanoic acid	96.5	1.8

[a] Carboxylic acid (200 mL), 2-(dinitromethylene)-4,5-imidazolidinedione (0.01mol), reaction 30 min, $T = 25$ °C.

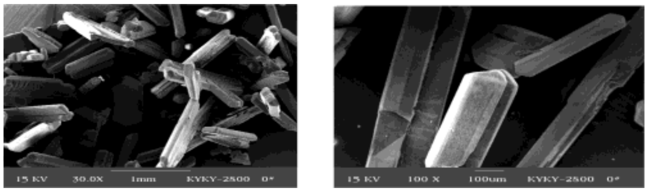
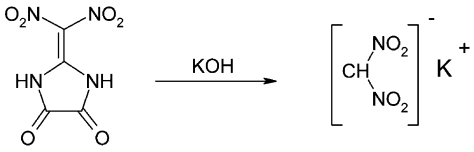


FIGURE 1. SEM photograph of **2** synthesized by ring cleavage of **1** by formic acid.

SCHEME 10



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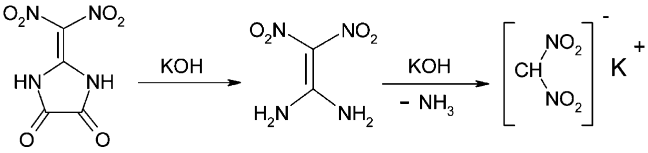
SCHEME 11



Sandberg studied hydrolysis of FOX-7 and found that **6** could be achieved under alkali conditions.[14] Thus, the possible mechanism was that FOX-7 formed first continued to decompose (see Scheme 11).

2.2 *gem*-Dinitro Reaction. *gem*-Dinitro compounds differed significantly in their thermal stability, and in some cases their structures were only postulated. Many of them are thermally unstable and easy to decompose. Examples of such decomposition can be found in the literature,[16−19] and carbonylation was usually achieved finally. According to ^{13}C NMR studies, Latypov confirmed that **1** underwent slow decomposition in DMSO to yield

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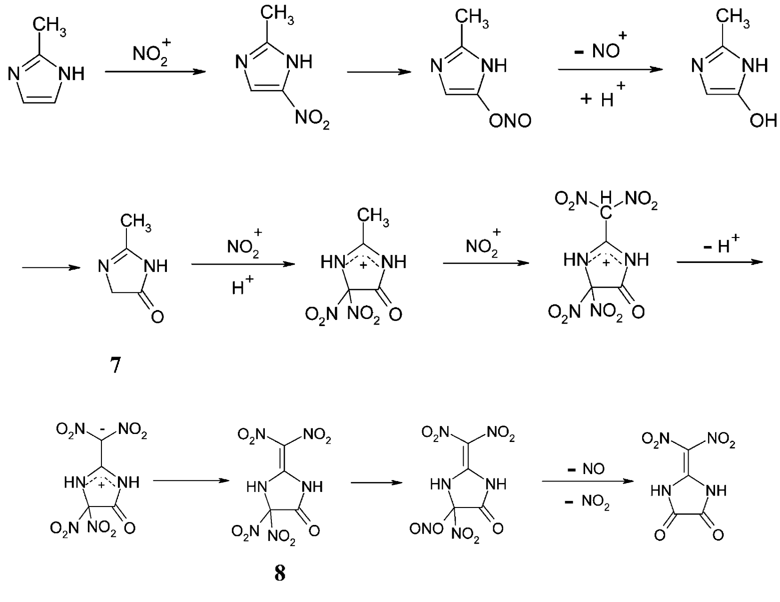
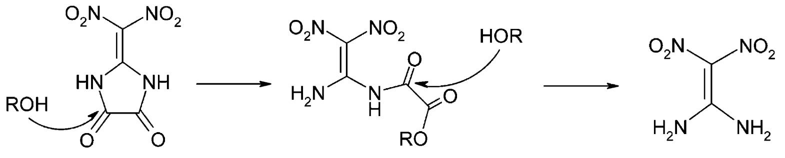
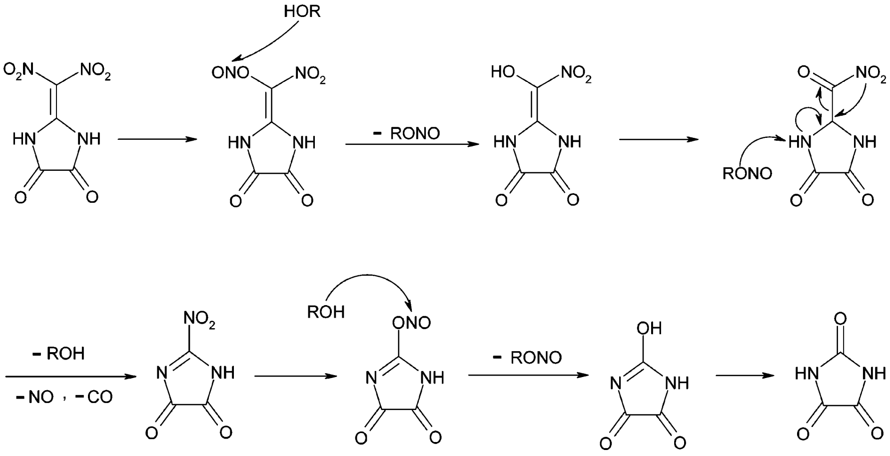
SCHEME 12



SCHEME 13



SCHEME 14



finally **5**.[1] In our experiments,[15] we found that **5** appeared as a major product or byproduct in almost all reactions of **1**. When **1** was placed in the air, it could absorb water and also undergo slow decomposition yielding finally a mixture of **2** and **5**. If methanol adduct (**4**) stands in a vacuum at ambient temperature for a long time, all of it could decompose into **5**, losing methanol, nitrogen monoxide, and carbon monoxide.

2.3. Explosive Decomposition. 2-(Dinitromethylene)-4,5-imidazolidinedione (**1**), with *gem*-dinitro, was a powerful and sensitive explosive, so it had some properties of explosive. In our experiments, we found that under certain conditions, for example, at high temperature, **1** can decompose rapidly to yield white gas products, and this exothermic explosive reaction has the capacity to cause a runaway reaction and in the worst case a deflagration. Under certain conditions, **4** can deflagrate as well.

2.4. Reaction Mechanism. 2.4.1. 2-(Dinitromethylene)-4,5-imidazolidinedione (1). We have discussed the reaction mechanism of **1** synthesized by low-temperature nitrations of 2-methylimidazole.[15] The key steps were rearrangement of nitro group and loss of nitrogen oxide (see Scheme 12). Compound **1** was formed mainly via two intermediates, 2-methyl-4,5-dihydro-5-imidazolone (**7**) and 2-(dinitromethylene)-5,5-dinitro-4-imidazolidinone (**8**), which have been discussed, analyzed, and proven thoroughly.

2.4.2. FOX-7 (2). We have also discussed the reaction mechanism of FOX-7 synthesized by ring cleavage of **1** by ammonium hydroxide.[15] The mechanism of ring cleavage by other reagents was similar to it. FOX-7 was formed mainly by the following steps (see Scheme 13): nucleophiles attacked the positive carbon of the carbonylation twice, with subsequent elimination of double carbonylations, and then FOX-7 was formed.

2.4.3. Parabanic Acid (5). The mechanism of parabanic acid formed was complex. We think that many steps are involved (see Scheme 14). The key steps were rearrangement of nitro group and elimination of carbon monoxide.

3. Conclusions

We have discovered some new reactions of **1** with water, alcohols, alkalis, and carboxylic acids. By reaction with carboxylic acids, large particle size FOX-7 (**2**) was prepared and might have applications in propellants and high explosive formulations. By reaction with KOH, potassium dinitromethane (**6**) was synthesized, which was a new route for it. By reaction with methanol, the methanol adduct of **1**, which was more stable than **1**, has been synthesized and characterized. The synthesis of adducts is important to theoretical research and future applications.

4. Experimental Section

General Methods. Melting points or decomposition temperatures were determined with DSC. Thermal sensitivity was measured with TG. IR spectra were measured by a spectrometer. ^{1}H and ^{13}C NMR spectra were recorded at 300 MHz (DMSO as solvent). Mass spectra were recorded by EI methods at 70 eV (the temperature of ion source was 200 °C, and the solid sample inlet was used). Elemental compositions were measured with an elemental analyzer. The features of FOX-7 were observed by SEM. The organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification.

Caution: All polynitro compounds described in this paper are explosives, and proper shielding is strongly recommended.

Formation of 2-(Dinitromethylene)-4,5-imidazolidinedione (1). Finely ground 2-methylimidazole 16.5 g (0.2mol) was dissolved in sulfuric acid (160 mL, 95%) at 19 °C with vigorous stirring. At the same temperature, nitric acid (32 mL, 1.51 g/L) was added over a 1.5 h period. After 1.5 h, a white precipitate was formed, which was collected and washed several times with cold trifluoroacetic acid. The precipitate was dried in a vacuum at 0 °C. On standing at room temperature for 5 h, 2-(dinitromethylene)-5,5-dinitro-4-imidazolidinone lost 26.5% of weight and gave 8.4 g (20.8%) of 2-(dinitromethylene)-4,5-imidazolidinedione: mp 240 °C dec (10 °C/min DSC); IR (KBr) 3313 (NH_2), 3226 (NH_2), 3169 (NH_2), 1805 (C=O), 1754 (C=O), 1584 (NO_2), 1499, 1318 (NO_2), 1232, 1176, 758 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 11.03 ppm; ^{13}C NMR (DMSO-d_6) δ 128.7, 154.7, 159.7; MS *m/z* 202 (M$^+$, 11.13), 138 (100), 69 (43.01), 30 (19.34). Anal. Calcd for $C_4H_2N_4O_6$: C, 23.77; H, 1.0; N, 27.72. Found: C, 23. 90; H, 1.23; N, 27.87.

Ring Cleavage of 1 to FOX-7 (2) by Water. 2-(Dinitromethylene)-4,5-imidazolidinedione (2.1 g, 0.01mol) was treated with dilute hydrogen chloride to form a mixture at 25 °C, and then the mixture was added to water dropwise. The white solid dissolved immediately, and in a few seconds bright yellow crystals precipitated. The crystals were washed with water and dried at 50 °C to give 1.2 g (81.1%) of FOX-7: mp 238 °C dec (7 °C/min DSC); IR (KBr) 3404 (NH_2), 3330 (NH_2), 3223 (NH_2), 1633 (NH_2), 1518 (NO_2), 1469, 1393, 1351 (NO_2), 1221, 1166, 1137, 1023, 620, 458 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 8.76 ppm; ^{13}C NMR (DMSO-d_6) δ 129.4, 159.0; MS *m/z* 148 (M$^+$, 84.01), 86 (21.34), 69 (38.36), 43 (100), 18 (72.01). Anal. Calcd for $C_2H_4N_4O_4$: C, 16.22; H, 2.72; N, 37.84. Found: C, 16.09; H, 2.68; N, 37.87.

Ring Cleavage of 1 to 2 by Methanol at Room Temperature. 2-(Dinitromethylene)-4,5-imidazolidinedione (2.1 g, 0.01mol) was dissolved in methanol at 25 °C with vigorous stirring. Fine iron powder and dilute hydrogen chloride (catalytic amount) were added to the solution. After 30 min, concentration of the solution gave the product as bright yellow crystals. The crystals were washed with water and dried at 50 °C to give 1.3 g (87.8%) of **2**. The product was spectroscopically (IR, NMR, and mass data) identical with previously prepared FOX-7.

Ring Cleavage of 1 to 2 by Methanol at High Temperature. 2-(Dinitromethylene)-4,5-imidazolidinedione (2.1 g, 0.01mol) was dissolved in methanol at 60 °Cwith vigorous stirring. After 30 min, the solution was concentrated slowly, and then bright yellow crystals precipitated. The precipitate was washed with water and dried at 50 °C to give 1.1 g (74.3%) of **2**. The product was spectroscopically (IR, NMR, and mass data) identical with previous prepared FOX-7.

Ring Cleavage of 2-Methylimidazole to 2 by Methanol. Finely ground 2-methylimidazole (16.5 g, 0.2 mol) was dissolved in sulfuric acid (95%, 160 mL) at 19 °C with vigorous stirring. At the same temperature, nitric acid (32 mL, 1.51 g/L) was added over a 1.5 h period. After 1.5 h, a white precipitate was formed. Methanol (200 mL) was added, and a yellow solution was formed. Concentration of the solution gave the product as bright yellow crystals. The crystals were washed with water and dried at 50 °C to give 12.2 g (41.2%) of **2**. The product was spectroscopically (IR, NMR, and mass data) identical with previously prepared FOX-7.

Ring Cleavage of 1 to 2 by Formic Acid. 2-(Dinitromethylene)-4,5-imidazolidinedione (2.1 g, 0.01mol) was dissolved in formic acid at 25 °C with vigorous stirring. After 30 min, the solution was concentrated slowly, and then bright yellow crystals precipitated. The crystals were washed with water and dried at 50 °C to give 1.4 g (94.6%) of **2**. IR, NMR, and mass data were identical with previously prepared FOX-7.

Under the same conditions, the yields of FOX-7 prepared by reactions of **1** with acetic acid, propanoic acid, *n*-butanoic acid, or *n*-pentanoic acid were 95.8%, 95.8%, 96.6%, or 96.5%, respectively.

Ring Cleavage of 1 to 2 by KOH. 2-(Dinitromethylene)-4,5-imidazolidinedione (2.1 g, 0.01 mol) was dissolved in 10 mL of water, and a solution of KOH (5%, 10 mL) was added dropwise to it at 25 °C. After 3 h, a yellow precipitate of FOX-7 was formed. The solution was concentrated slowly, and then bright yellow crystals precipitated. The crystals were collected, washed with water, and dried at 50 °C to give 1.3 g (87.8%) of **2**. IR, NMR, and mass data were identical with previous prepared FOX-7.

Methanol Adduct of 2-(Dinitromethylene)-4,5-imidazolidinedione (4). 2-(Dinitromethylene)-4,5-imidazolidinedione (2.1 g, 0.01mol) was dissolved in 200 mL of methanol at ambient temperature with vigorous stirring. Fine iron powder and dilute hydrogen chloride (catalytic amount) were added to the solution. After 30 min, the solution was concentrated slowly, and then yellow needle crystals precipitated. The crystals were washed with water and dried at 50 °C to give 2.3 g (98.3%) of **4**: mp 140.0−140.9 °C; IR (KBr) 3362 (NH_2), 3249 (NH_2), 1753 (C=O), 1734 (C=O), 1618 (NH_2), 1575 (NO_2), 1475, 1323 (NO_2), 1230, 1140, 964 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 3.69, 8.81, 11.76 ppm; ^{13}C NMR (DMSO-d_6) δ 48.7, 53.5, 100.4, 128.7, 154.9, 159.8; MS *m/z* 234 (M$^+$, 36.14), 188 (100), 175 (40.15), 138 (71.05), 112 (53.12), 69 (75.01), 59 (69.89).; Anal. Calcd for $C_5H_6N_4O_7$: C, 25.64; H, 2.56; N, 23.93. Found: C, 25.70; H, 2.64; N, 24.07.

Ring Cleavage of 1 to Potassium Dinitromethane (6) by KOH. 2-(Dinitromethylene)-4,5-imidazolidinedione (2.1 g, 0.01mol) was dissolved in a solution of KOH (10%,40 mL) at 15 °C. The resulting solution was warmed to 70−95 °C and was kept at this temperature. After 3 h, when the evolution of ammonia ceased, the solution was cooled to 15 °C and the pale yellow product formed was collected by filtration, washed with water, and dried at 50 °C to give 0.94 g (65.3%) of **6**: mp 220 °C dec; UV $\lambda_{max} = 363$ nm; $\epsilon = 20\,800$.

Parabanic Acid (5). 2-(Dinitromethylene)-4,5-imidazolidinedione (2.1 g, 0.01mol) was dissolved in 200 mL of methanol at 0 °C with vigorous stirring. Fine iron powder and dilute hydrogen chloride (catalytic amount) were added to the solution. After 30 min, the solution was concentrated slowly, and then the white solids precipitated. The precipitate proved to be a mixture of parabanic acid and **4**, which were dissolved in water, and the insoluable **4** was filtrated (0.3 g, 12.8%). The filtrate was condensed, and cooling to 10 °C and keeping overnight resulted in the precipitation of 0.17 g (14.9%) of **5**.

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