Reaction of β-Nitroketeneaminal with Olefins Bearing Electron-Withdrawing Group and Aldehydes

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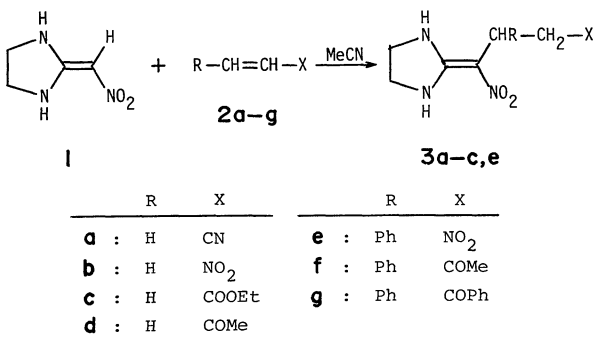
The reaction of 2-(nitromethylene)imidazolidine (**1**) with olefins bearing an electron-withdrawing group gave Michael-type addition products and/or 5-nitro-1,7-diazabicyclo[4.3.0]nonane derivatives derived from the Michael-type adduct. The reaction of **1** with α,β-unsaturated aldehydes in the presence of an acid, on the other hand, gave similar diazabicyclic derivatives and 2-[(2-imidazolidinylidene)nitromethylene]-5-nitro-1,7-diazabicyclo[4.3.0]non-5-ene derivatives. The reaction of **1** with saturated and aromatic aldehydes in the presence of hydrochloric acid gave 1,3-bis(2-imidazolidinylidene)-1,3-dinitropropane derivatives. The enhanced enaminic character of **1** is ascribable to the two electron-donating amino groups fixed in a five-membered ring.

In previous papers the author reported that β-nitroenamines reacted with some electrophiles to give β-substituted β-nitroenamines and heterocyclic compounds.[1,2] However, the nucleophilic reactivity of the β-nitroenamines is so small that they do not react with the carbon-electrophiles, such as aldehydes, except formaldehyde, which reacts with *N*-phenyl β-nitroenamine to give an aldol adduct,[3] and olefins bearing an electron-withdrawing group. On the other hand, Rajappa suggested that β-nitroketeneaminals with two amino groups at the β-position of nitroethylene may possess a moderate enaminic reactivity, owing to the electron-donating character of two amino groups.[4,5]

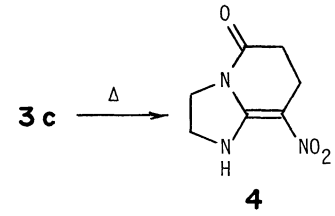
In this paper I wish to report that 2-(nitromethylene)imidazolidine (**1**) reacts with olefins bearing an electron-withdrawing group or aldehydes to give products arising from Michael or aldol adducts.

Results and Discussion

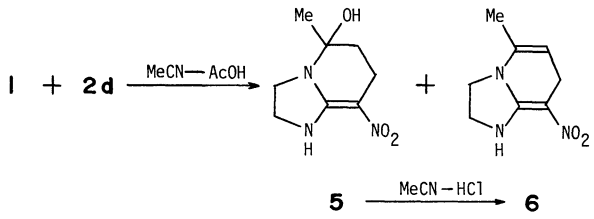
Reaction of 2-(Nitromethylene)imidazolidine (1) with Olefins 2. The reaction of imidazolidine **1** with olefins **2a,b,e** in acetonitrile gave β-substituted β-nitroketeneaminals **3a,b,e** in 67.7—95% yields. Ethyl acrylate (**2c**) afforded the Michael adduct **3c** together with a small amount of lactam **4** arising from cyclization of **3c**; β-nitroketeneaminal **3c** gave lactam **4** (94%) upon heating for a few minutes at 160 °C (Scheme 2). Imidazolidine **1** and 3-buten-2-one (**2d**) in acetonitrile containing a catalytic amount of acetic acid gave a cyclized adduct **5** and its dehydration product **6** in 63.6 and 22% yields. Product **5** was dehydrated to give product **6** in 90% yield upon refluxing for 3 min in acetonitrile containing a catalytic amount of hydrochloric acid (Scheme 3). In the reaction with olefins **2f,g** under similar conditions, products **7** and **8** arising from a Michael addition,



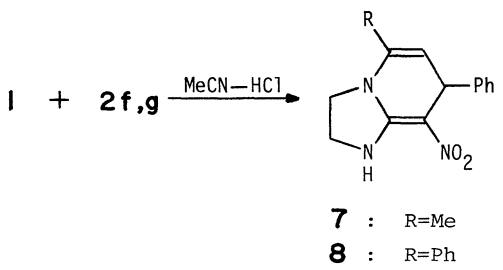
Scheme 1.



Scheme 2.



Scheme 3.

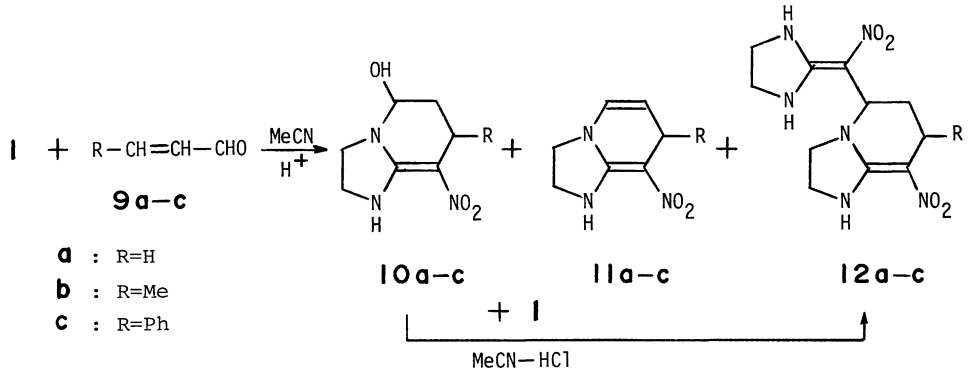


Scheme 4.

Table 1. Reaction of **1** with α,β-Unsaturated Aldehydes **9**

9	Catalyst	Reaction temp/°C	Reaction time/h	Product					
				10		11		12	
				Yield/%	Mp/°C	Yield/%	Mp/°C	Yield/%	Mp/°C
9a	HCl	40	8	56	159—160	35	153—154	—	
9b	AcOH	Bp	15	62.8	161—162	—		—	
9b[a)]	HCl	Bp	8	—		16.5	141—142	51.5	264—265
9c	AcOH	Bp	24	32.9	226	—		—	
9c	HCl	Bp	8	6	226	6	175—176	86.9	278

a) Used 2 equimolar amounts of **1**.

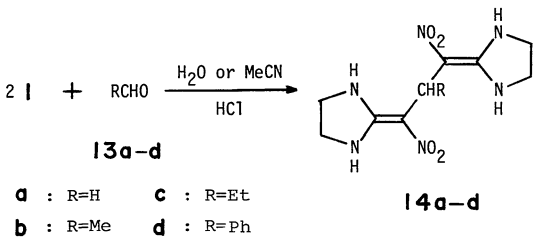


Scheme 5.

Table 2. Reaction of **1** with Aldehydes **13**

13	Solvent	Catalyst	Reaction temp/°C	Reaction time/h	Product	Yield/%[a)]	Mp/°C
13a	H_2O	HCl	Rt	5	**14a**	74.0	254
13b	H_2O	HCl	Rt	24	**14b**	71.8	221
13c	MeCN	HCl	Bp	2	**14c**	85.8	230
13d	MeCN	HCl	Bp	5	**14d**	83.8	226

a) Recrystallized from DMF.



Scheme 6.

followed by dehydration were exclusively obtained in 56 and 59% yields, respectively; none of the β-substituted β-nitroketeneaminals were obtained (Scheme 4). Similar reactions of **1** with α,β-unsaturated aldehydes **9a—c** in acetonitrile containing a catalytic amount of acetic acid or hydrochloric acid afforded mixtures of adducts **10a—c**, their dehydration products (**11a—c**) and compounds (**12b,c**) formed via condensation of **10b,c** with **1**, without any formation of aldol adducts (Scheme 5). The results are summarized in Table 1. The isolated **10a—c** was dehydrated upon refluxing in 1,2-dichloroethane containing acetic acid (10%) to give the corresponding **11a—c** in 87—89.6% yields. The reaction of products **10a—c** with **1** in the presence of hydrochloric acid gave **12a—c** in 64.6—87% yields. The results show that the Michael addition takes place in preference to the aldol reaction.

Reaction of 2-(Nitromethylene)imidazolidine (1) with Aldehydes 13. The addition reaction of imidazolidine **1** with α,β-unsaturated aldehydes **9a—c** (as described above) gave predominantly Michael-type adducts. Aliphatic or aromatic aldehydes **13a—d**, however, reacted with imidazolidine **1** in the presence of hydrochloric acid as a catalyst to give 1:2 condensation products (**14a—d**) in 71.8—85.8% yields (Scheme 6). The results are summarized in Table 2. Products **14a—d** are presumably formed via aldol

addition, acid-catalyzed dehydration, and the final addition of **1** to the resulting iminium intermediate.

Thus, the enhanced reactivity of 2-(nitromethylene)-imidazolidine (**1**) described above may be attributable to an enhanced enaminic character by the two electron-donating amino groups. The reaction of acyclic β-nitroketeneaminals, such as *N,N'*-dimethyl β-nitroketeneaminal, with olefins bearing an electron-withdrawing group and aldehydes, however, led to the recovery of unchanged starting materials or a mixture of decomposition products. Thus, the reactivity of β-nitroketeneaminals depends on the structure. The greater nucleophilicity of **1** may presumably to be due to fixed C–N bonds in the five-membered ring.

Experimental

The melting points are uncorrected. IR and UV spectra were measured with Hitachi 270-50 and Hitachi 124 spectrophotometers, respectively. The ^{1}H NMR spectra were recorded with a Hitachi R-24B (60 MHz) or a R-250H (250 MHz) instrument using TMS as an internal standard. Elemental analyses were performed at the Microanalytical Laboratory of Kyoto University.

Materials. 2-(Nitromethylene)imidazolidine (**1**) and nitroethylene were prepared according to the reported procedures.[6,7] The other reagents commercially available were used without further purification.

Reaction of 1 with Olefins 2. A solution containing **1** (5 mmol) and **2a—c,e** (5.5 mmol) in acetonitrile 15 ml was heated under reflux for 1—72 h. After the solvent was removed by a rotary evaporator the residue was purified by recrystallization to give **3a—c,e.**

2-(3-Cyano-1-nitropropylidene)imidazolidine (3a): Reaction time 72 h; yield 86.8% (from DMF); mp 197 °C; IR (KBr) 3360 m, 3200 m, 2225 m, 1605 s, 1543 s, and 1340 s cm^{-1}; UV (EtOH) λ_{nm} ($10^{-4}\varepsilon$) 338 (2.0); ^{1}H NMR (DMSO-d_6) δ=8.55 (br, 2H), 3.70 (s, 4H), 2.82 (t, J=5 Hz, 2H), and 2.60 (t, J=5 Hz, 2H). Found: C, 46.03; H, 5.47; N, 30.82%. Calcd for $C_7H_{10}N_4O_2$: C, 46.15; H, 5.53; N, 30.75%.

2-(1,3-Dinitropropylidene)imidazolidine (3b): Reaction time 4 h; yield 67.7% (from acetonitrile); mp 188 °C; IR (KBr) 3350 m, 3200 m, 1598 s, 1562 s, 1545 s, 1365 s, and 1338 s cm^{-1}; UV (EtOH) λ nm ($10^{-4}\varepsilon$) 328 (1.9); ^{1}H NMR (DMSO-d_6) δ=8.55 (br, 2H), 4.56 (t, J=7 Hz, 2H), 3.67 (s, 4H), and 3.10 (t, J=7 Hz, 2H). Found: C, 35.70; H, 4.82; N, 27.70%. Calcd for $C_6H_{10}N_4O_4$: C, 35.65; H, 4.98; N, 27.71%.

2-(3-Ethoxycarbonyl-1-nitropropylidene)imidazolidine (3c): Reaction time 36 h; yield 55.0% (from EtOH); mp 157 °C; IR (KBr) 3330 m, 3200 m, 1728 s, 1604 s, 1540 s, 1366 s, 1351 s, and 1318 s cm^{-1}; UV (EtOH) λ nm ($10^{-4}\varepsilon$) 346 (2.0); ^{1}H NMR (DMSO-d_6) δ=8.50 (br, 2H), 4.90 (q, J=7 Hz, 2H), 3.67 (s, 4H), 2.70 (m, 4H), and 1.20 (t, J=7Hz, 3H). Found: C, 46.89; H, 6.31; N, 18.29%. Calcd for $C_9H_{15}N_3O_4$: C, 47.15; H, 6.59; N, 18.33%.

2-(1,3-Dinitro-2-phenylpropylidene)imidazolidine (3e): Reaction time 1 h; yield 95% (from acetonitrile); mp 195 °C; IR (KBr) 3330 m, 3220 m, 1593 s, 1551 s, 1542 s, 1374 s, and 1342 s cm^{-1}; UV (EtOH) λ nm ($10^{-4}\varepsilon$) 329 (1.9); ^{1}H NMR (DMSO-d_6) δ=8.80 (br, 2H), 7.28 (s, 5H), 5.37 (d, J=7 Hz, 2H), 4.67 (t, J=7 Hz, 1H), and 3.70 (s, 4H). Found: C, 51.80; H, 5.03; N, 19.93%. Calcd for $C_{12}H_{14}N_4O_4$: C, 51.79; H, 5.07; N, 20.13%.

The isolated **3c** was heated at 160 °C for 3 min, and recrystallized from ethanol to afford 5-nitro-1,7-diazabicyclo-[4.3.0.]non-5-en-2-one (**4**) in a 91% yield; mp 245 °C (decomp); IR (KBr) 3350 m, 1695 s, 1640 s, 1488 s, 1348 s, and 1313 s cm^{-1}; UV (EtOH) λ nm ($10^{-4}\varepsilon$) 349 (2.2); ^{1}H NMR (DMSO-d_6) δ=9.49 (br, 1H), 3.82 (s, 4H), and 2.73 (m, 4H). Found: C, 46.19; H, 4.94; N, 23.01%. Calcd for $C_7H_9N_3O_3$: C, 45.90; H, 4.95; N, 22.94%.

The reaction of **1** with **2d** was carried out in acetonitrile containing of a catalytic amount of acetic acid; after heating under reflux for 2 h, the mixture was cooled, and the resulting precipitation was separated by filtration to give 2-methyl-5-nitro-1,7-diazabicyclo[4.3.0]non-5-en-2-ol (**5**): yield 63.6% (from acetonitrile); mp 183—184 °C (decomp); IR (KBr) 3320 m, 3180 m, 1595 s, 1532 s, 1380 s, and 1340 s cm^{-1}; UV (EtOH) λ nm ($10^{-4}\varepsilon$) 338 (1.8); ^{1}H NMR (DMSO-d_6) δ=9.0 (br, 1H), 5.90 (s, 1H), 3.65 (s, 4H), 2.60 (m, 2H), 1.95 (m, 2H), and 1.50 (s, 3H). Found: C, 48.06; H, 6.51; N, 20.86%. Calcd for $C_8H_{13}N_3O_3$: C, 48.23; H, 6.58; N, 21.09%. The filtrate was evaporated; the residue was then purified by recrystallization from benzene to give 2-methyl-5-nitro-1,7-diazabicyclo[4.3.0]nona-2,5-diene (**6**), which was the dehydration product of **5**: yield 22%; mp 138—139 °C; IR (KBr) 3300 m, 1683 m, 1660 s, 1530 s, and 1365 s cm^{-1}; UV (EtOH) λ nm ($10^{-4}\varepsilon$) 311 (1.0) and 374 (1.5); ^{1}H NMR ($CDCl_3$) δ=8.9 (br, 1H), 4.90 (m, 1H), 3.70 (s, 4H), 3.37 (m, 2H), and 1.90 (d, J=2Hz, 3H). Found: C, 52.91; H, 5.99; N, 23.07%. Calcd for $C_8H_{11}N_3O_2$: C, 53.03; H, 6.12; N, 23.19%. On the other hand, the isolated **5** (5 mmol) was refluxed in 10 ml of acetonitrile containing a drop of concentrated hydrochloric acid for 3 min to give **6** in a 90% yield.

The reaction of **1** with **2f,g** was performed in the same manner as **2d** by adding a catalytic amount of concentrated hydrochloric acid. The reaction with **2f** was stirred under reflux for 40 h, and the solvent was evaporated; the residue was then recrystallized from ethanol to afford 2-methyl-5-nitro-4-phenyl-1,7-diazabicyclo[4.3.0]nona-2,5-diene (**7**): yield 59.1%; mp 194—195 °C; IR (KBr) 3320 m, 1683 m, 1598 s, 1495 s, 1365 s, and 1321 s cm^{-1}; UV (EtOH) λ nm ($10^{-4}\varepsilon$) 320 (1.5) and 368 (1.1); ^{1}H NMR ($CDCl_3$) δ=8.60 (br, 1H), 7.25 (s, 5H), 4.93 (d, J=6 Hz, 1H), 4.77 (d, J=6Hz, 1H), 3.80 (m, 4H), and 1.9 (s, 3H). Found: C, 65.35; H, 5.79; N, 16.06%. Calcd for $C_{14}H_{15}N_3O_2$: C, 65.35; H, 5.87; N, 16.33%. Similarly, the reaction with **2g** was heated under reflux for 6 h to give the corresponding 5-nitro-2,4-diphenyl-1,7-diazabicyclo[4.3.0]-nona-2,5-diene (**8**): yield 55.1% (from EtOH); mp 176—177 °C; IR (KBr) 3350 m, 1660 s, 1610 s, 1496 s, 1358 s, and 1328 s cm^{-1}; UV (EtOH) λ nm ($10^{-4}\varepsilon$) 323 (1.3) and 369 (1.2); ^{1}H NMR ($CDCl_3$) δ=8.70 (br, 1H), 7.28 (m, 10H), 5.15 (d, J=4 Hz, 1H), 4.95 (d, J=4 Hz, 1H), and 3.60 (m, 4H). Found: C, 71.34; H, 5.19; N, 13.10%. Calcd for $C_{19}H_{17}N_3O_2$: C, 71.45; H, 5.36; N, 13.15%.

Reaction of 1 with α,β-Unsaturated Aldehydes 9a—c. A solution containing **1**(5 mmol), **9a—c** (5.5 or 11 mmol) and a catalytic amount of acetic acid or concentrated hydrochloric acid in 15 ml of acetonitrile was stirred at 40 °C for 8 h or under reflux for 8—24 h. The solvent was removed by a rotary evaporator, and the residue was sepatated by silica-gel columun chromatography (dichloromethane–acetone 5:1) or fractional precipitation (from DMF). The results are

summarized in Table 1.

5-Nitro-1,7-diazabicyclo[4.3.0]non-5-en-2-ol (10a): IR (KBr) 3350 m, 3150 m, 1600 s, 1530 s, and 1345 s cm^{-1}; UV (EtOH) λ nm ($10^{-4}\varepsilon$) 336 (2.2); ^1H NMR (DMSO-d_6) δ=9.1 (br, 1H), 6.20 (d, J=6 Hz, 1H), 5.0 (m, 1H), 3.71 (m, 4H), 2.65 (m, 2H), and 1.90 (m, 2H). Found: C, 45.40; H, 5.90; N, 22.52%. Calcd for $C_7H_{11}N_3O_3$: C, 45.40; H, 5.98; N, 22.69%.

4-Methyl-5-nitro-1,7-diazabicyclo[4.3.0]non-5-en-2-ol (10b): IR (KBr) 3300 m, 3160 m, 1587 s, 1531 s, and 1368 s cm^{-1}; UV (EtOH) λ nm ($10^{-4}\varepsilon$) 336 (2.2); ^1H NMR (DMSO-d_6) δ=8.9 (br, 1H), 6.30 (d, J=7 Hz, 1H), 4.83 (m, 1H), 3.68 (m, 4H), 3.15 (m, 1H), 1.85 (m, 2H), and 1.12 (d, J=5 Hz, 3H). Found: C, 48.25; H, 6.51; N, 20.86%. Calcd for $C_8H_{13}N_3O_3$: C, 48.23; H, 6.57; N, 21.09%.

5-Nitro-4-phenyl-1,7-diazabicyclo[4.3.0.]non-5-en-2-ol (10c): IR (KBr) 3320 m, 3180 m, 1603 s, 1523 s, and 1368 s cm^{-1}; UV (EtOH) λ nm ($10^{-4}\varepsilon$) 335 (2.2); ^1H NMR (DMSO-d_6) δ=9.1 (br, 1H), 7.25 (m, 5H), 6.40 (d, J=7 Hz, 1H), 4.40 (m, 2H), 3.72 (m, 4H), and 2.05 (m, 2H). Found: C, 59.62; H, 5.68; N, 16.09%. Calcd for $C_{13}H_{15}N_3O_3$: C, 59.76; H, 5.78; N, 16.08%.

5-Nitro-1,7-diazabicyclo[4.3.0]nona-2,5-diene (11a): IR (KBr) 3330 m, 1665 m, 1605 s, 1502 s, and 1350 s cm^{-1}; UV (EtOH) λ nm ($10^{-4}\varepsilon$) 306 (0.6) and 373 (1.4); ^1H NMR ($CDCl_3$) δ=8.9 (br, 1H), 6.30 (d, J=8 Hz, 1H), 5.20 (m, 1H), 3.90 (s, 4H), and 3.45 (m, 2H). Found: C, 50.18; H, 5.39; N, 25.05%. Calcd for $C_7H_9N_3O_2$: C, 50.29; H, 5.42; N, 25.13%.

4-Methyl-5-nitro-1,7-diazabicyclo[4.3.0]nona-2,5-diene (11b): IR (KBr) 3330 m, 1665 s, 1591 s, 1505 s, 1365 s, and 1340 s cm^{-1}; UV (EtOH) λ nm ($10^{-4}\varepsilon$) 311 (0.6) and 372 (1.1); ^1H NMR ($CDCl_3$) δ=8.5 (br, 1H), 5.91 (d, J=8 Hz, 1H), 5.03 (dd, J=8 and 6 Hz, 1H), 3.85 (m, 4H), 3.67 (m, 1H), and 1.25 (d, J=7 Hz, 3H). Found: C, 53.08; H, 6.07; N, 23.15%. Calcd for $C_8H_{11}N_3O_2$: C, 53.03; H, 6.12; N, 23.12%.

4-Phenyl-5-nitro-1,7-diazabicyclo[4.3.0]nona-2,5-diene (11c): IR (KBr) 3370 m, 1668 s, 1603 s, 1594 s, 1505 s, 1358 s, and 1340 s cm^{-1}; UV (EtOH) λ nm ($10^{-4}\varepsilon$) 315 (0.6) and 367 (1.1); ^1H NMR ($CDCl_3$) δ=8.5 (br, 1H), 7.30 (m, 5H), 6.0 (d, J=8 Hz, 1H), 5.15 (dd, J=8 and 6 Hz, 1H), 4.13 (d, J=5 Hz, 1H), and 3.69 (m, 4H). Found: C, 64.12; H, 5.18; N, 17.04%. Calcd for $C_{13}H_{13}N_3O_2$: C, 64.18; H, 5.38; N, 17.28%.

Reaction of 1 with Isolated 10a—c. A solution containing **1** (5 mmol), **10a—c** (5 mmol) and a catalytic amount of concentrated hydrochloric acid in 15 ml of acetonitrile was stirred under reflux for 5 h. After cooling, the resulting precipitation was removed by filtration; the residue was then recrystallized from DMF to give the condensation products **12a—c**, respectively. The results are as follows.

2-[(2-Imidazolidinylidene)nitromethylene]-5-nitro-1,7-diazabicyclo[4.3.0]non-5-ene (12a): Yield 86%; mp 283 °C (decomp); IR (KBr) 3350 m, 3270 m, 1604 s, 1584 s, 1366 s, and 1340 s cm^{-1}; UV (EtOH) λ nm ($10^{-4}\varepsilon$) 332 (4.0); ^1H NMR (DMSO-d_6) δ=9.1 (br, 1H), 8.9 (br, 2H), 4.55 (m, 1H), 3.70 (m, 4H), 3.50 (m, 4H), 2.78 (m, 2H), and 1.83 (m, 2H). Found: C, 44.61; H, 5.36; N, 27.99%. Calcd for $C_{11}H_{16}N_6O_4$: C, 44.59; H, 5.44; N, 28.36%.

2-[(2-Imidazolidinylidene)nitromethylene]-4-methyl-5-nitro-1,7-diazabicyclo[4.3.0]non-5-ene (12b): Yield 64.6%; mp 264—265 °C (decomp); IR (KBr) 3340 m, 3290 m, 1590 s, 1540 s, 1526 s, 1362 s, and 1328 s cm^{-1}; UV (EtOH) λ nm ($10^{-4}\varepsilon$) 333 (4.2); ^1H NMR (DMSO-d_6) δ=9.1 (br, 1H), 8.7 (br, 2H), 4.32 (m, 1H), 3.60 (m, 8H), 1.51 (m, 2H), and 1.19 (d, J=7 Hz, 3H). Found: C, 46.41; H, 5.74; N, 27.02%. Calcd for $C_{12}H_{18}N_6O_4$: C, 46.44; H, 5.84; N, 27.08%.

2-[(2-Imidazolidinylidene)nitromethylene]-5-nitro-4-phenyl-1,7-diazabicyclo[4.3.0]non-5-ene (12c): Yield 87%; mp 278 °C (decomp); IR (KBr) 3320 m, 3200 m, 1599 s, 1580 s, 1377 s, and 1365 s cm^{-1}; UV (EtOH) λ nm ($10^{-4}\varepsilon$) 333 (4.1); ^1H NMR (DMSO-d_6) δ=9.1 (br, 1H), 8.5 (br, 2H), 7.35 (m, 5H), 4.35 (m, 2H), 3.60 (m, 8H), and 1.80 (m, 2H). Found: C, 54.67; H, 5.34; N, 22.55%. Calcd for $C_{17}H_{20}N_6O_4$: C, 54.78; H, 5.40; N, 22.64%.

Reaction of 1 with Aldehydes 13a—d. A solution containing **1** (5 mmol), **13a—d** (2.5 mmol) and a catalytic amount of hydrochloric acid in water or acetonitrile 15 ml was stirred at room temperature for 5—25 h or under reflux for 2 h. After cooling, thr reaction mixture was neutralized with triethylamine. The resulting precipitation was filtered off and washed with water, and recrystallized from DMF to give **14a—d**. The results are summarized in Table 2.

1,3-Bis(2-imidazolidinylidene)-1,3-dinitropropane (14a): IR (KBr) 3350 m, 3310 m, 1604 s, 1543 s, 1375 s, and 1367 s cm^{-1}; UV (EtOH) λ nm ($10^{-4}\varepsilon$) 316 (2.4); ^1H NMR (DMSO-d_6) δ=9.1 (br, 4H), 3.95 (s, 2H), 3.77 (s, 8H), Found: C, 39.92; H, 5.20; N, 30.79%. Calcd for $C_9H_{14}N_6O_4$: C, 40.00; H, 5.22; N, 31.09%.

1,3-Bis(2-imidazolidinylidene)-2-methyl-1,3-dinitropropane (14b): IR (KBr) 3330 m, 3180 m, 1588 s, 1530 s, 1345 s, and 1320 s cm^{-1}; UV (EtOH) λ nm ($10^{-4}\varepsilon$) 322 (2.2); ^1H NMR (DMSO-d_6) δ=9.1 (br, 4H), 4.88 (q, J=8 Hz, 1H), 3.73 (s, 8H), and 1.48 (d, J=8 Hz, 3H). Found: C, 42.03; H, 5.58; N, 29.60%. Calcd for $C_{10}H_{16}N_6O_4$: C, 42.25; H, 5.67; N, 29.56%.

1-(2-Imidazolidinylidene)-2-[(2-imidazolidinylidene)nitromethyl]-1-nitrobutane (14c): IR (KBr) 3350 m, 3330 m, 1531 s, 1379 s, 1355 s, and 1325 s cm^{-1}; UV (EtOH) λ nm ($10^{-4}\varepsilon$) 322 (2.2); ^1H NMR (DMSO-d_6) δ=9.0 (br, 4H), 4.50 (t, J=8 Hz, 1H), 3.65 (s, 8H), 1.86 (m, 2H), and 0.68 (t, J=8 Hz, 3H). Found: C, 44.64; H, 6.03; N, 28.11%. Calcd for $C_{11}H_{18}N_6O_4$: C, 44.82; H, 6.08; N, 28.17%.

1,3-Bis(2-imidazolidinylidene)-1,3-dinitro-2-phenylpropane (14d): IR (KBr) 3330 m, 3250 m, 1607 s, 1524 s, 1370 s, and 1340 s cm^{-1}; UV (EtOH) λ nm ($10^{-4}\varepsilon$) 323 (2.2); ^1H NMR (DMSO-d_6) δ=8.9 (br, 4H), 7.2 (m, 5H), 6.2 (s, 1H), and 3.70 (s, 8H). Found: C, 52.01; H, 5.30; N, 24.05%. Calcd for $C_{15}H_{18}N_6O_4$: C, 52.02; H, 5.24; N, 24.26%.

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