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N-NITROSO AND N-NITRO DERIVATIVES OF DIAZACYCLOALKANES AND TETRAAZABICYCLOALKANES FROM α,α'-DIAMINODICARBOXYLATE ESTERS

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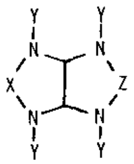
Abstract—A synthesis of 6,8-dinitro-2,4,6,8-tetraaza[3.3.1]bicyclononan-3-one 5c from dimethyl α,α'-diaminoglutarate 7 was brought about in six steps. A similar conversion of dimethyl α,α'-diaminosuccinate 8 to a derivative of 2,4,6,8-tetraaza[3.3.0]bicyclooctane 6 was unsucessful.

INTRODUCTION

In the continuing search for superior energetic materials to offer improvements in explosives and propellants the successful utilization of monocyclic oligomeric nitrimines, e.g., $[CH_2N(NO_2)]_x$ where x = 3 (RDX) and x = 4 (HMX), has been widespread.[1] There has been limited success in the synthesis of examples of related poly N-nitro derivatives of bi- and tri-cyclic polyazaalkanes and -alkanones (ureas). The compound 2,4,6,8-tetranitro-2,4,6,8-tetraaza[3.3.0]bicyclooctan-2-one 1,[2] -3,7-dione 2,[3] the 3,3,7,7-tetratrifluoromethyl-2,4,6,8-tetranitro-2,4,6,8-tetraazabicyclooctane 3,[4] and 2,4,-10-trinitro-2,4,10-triazaadamantane 4 [5] were obtained by methods that have not afforded generality. An enhancement in the energetic properties of poly N-nitramines to be expected from condensed and caged ring structures is dependent on the development of new preparative methods for polyazacycloalkane and -polycycloalkane systems. This report describes conversions of α,α'-diaminodicarboxylate esters to di-N-nitrosodiazacycloalkane derivatives and a synthesis of a tetraazabicycloalkane system 5 designed to contain neither N-N ring bonds nor nitrogen atoms at bridgehead positions.

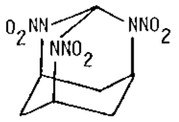


1 X = CH_2, Z = CO, Y = NO_2

2 X = Z = CO, Y = NO_2

3 X = Z = $C(CF_3)_2$, Y = NO_2

6 X = Z = CH_2, Y = H



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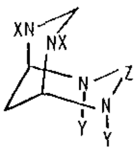


5a X = Y = H, Z = CH_2

5b X = NO, Y = H, Z = CO

5c X = NO_2, Y = H, Z = CO

5d X = Y = H, Z = CO

5e X = Y = NO_2, Z = CO

RESULTS AND DISCUSSION

Syntheses of the unknown 2,4,6,8-tetraaza[3.3.1]bicyclononane and 2,4,6,8-tetraaza[3.3.0]bicyclooctane ring systems 5a and 6 from diamino-glutarate 7 and -succinate 8 were investigated. Just as the 1,3-dinitroso derivatives of hexahydropyrimidine and imidazolidine were obtained from trimethylenediamine and from ethylenediamine by ring-closure condensations with formaldehyde followed by nitrosations,[6] the dimethyl esters 9 of a mixture of cis- and trans-1,3-dinitrosohexahydropyrimidine-4,6-dicarboxylates and dimethyl cis-1,3-dinitrosoimidazolidine-4,5-dicarboxylate 18 were obtained from a mixture of dimethyl threo- and erythro- α,α'-diaminoglutarate 7 and from dimethyl or diethyl meso-diaminosuccinate 8.

The bicyclic dinitrourea 5c was obtained from the mixture 9 by a straightforward sequence of reactions with (1) hydrazine to give a mixture of cis- and trans-hydrazides 10 from which the cis-isomer was separated by fractional crystallization, (2) nitrous acid to convert the cis-hydrazide 10 to the corresponding cis-diazide 11, (3) thermolysis to give an unisolated cis-bisisocyanate 12, (4) hydrolysis with ring closure, and (5) conversion of the bicyclic dinitrosamine 5b with nitric acid (100%) to the dinitramine 5c.

An inconvenience in the isolation of the bisisocyanate 12 was reminiscent of other Curtius reactions on vicinal diazides, the tendency of a bisisocyanate to polymerize,[7] and the preferred isolation of either a cyclic urea, e.g. 5b, when the unisolated bisisocyanate reacted with water, or a carbamate. After the diazide 11 was heated in benzene at 80°C and combined with ethanol the dicarbamate 13 was obtained. Unsuccessful attempts to bring about conversion to a derivative of tetraazabicyclononane from a reaction between the dicarbamate 13 and formaldehyde or an equivalent reagent revealed a resistance to an intermolecular ring closure not shared with the intramolecular cyclization that readily occurred when the bisisocyanate 12 and water gave the bicyclic urea 5b.

Presumably a conversion of the dinitrosamine 5b to a dinitramine 5c was another example of the replacement of a nitroso group with, rather than oxidation to, a nitro group in a reaction with nitric acid.[8] In contrast with N,N'-dinitration of simple cyclic ureas by treatment with either nitric acid in acetic anhydride or with dinitrogen pentoxide[9] attempts to N-nitrate the urea portion of the heterocycles 5b,c have been unsuccessful. A search for a conversion of the dinitramine 5c to the tetranitro compound 5e is underway.

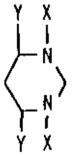
In a similar reaction nitric acid (100%) converted the dinitrosamine 9 to the cis-dinitramine 14 that gave the cis-dicarboxylic acid 15 on hydrolysis. Attempts to convert the acid to the diamine 16 by treatment with diphenylphosphoryl azide[10] gave instead an intractable mixture. Unsuccessful attempts to obtain an acid chloride or an acid anhydride from the acid 15 and ethyl chloroformate, or phosphorous pentachloride, or thionyl chloride precluded further conversion to the hydrazide 17. In contrast with the preparation of the hydrazide 10 from the diester 9, hydrazine reacted with the diester 14 to give an unstable mixture that did not contain the dihydrazide 17 in a detectable amount. The occurrence of a competitive base catalysed elimination of the elements of nitrous acid to give pyrimidine and hydropyrimidine derivatives was assumed since a comparable elimination accounted for the formation of imidazoles from 1,3-dinitroimidazolidines (see below). These results suggested that an elimination of nitrous acid from a 1,3-dinitro-1,3-diazaheterocycle can occur more readily than an elimination of nitroxyl from a *1,3-dinitroso-1,3-diazaheterocycle*.

An intention to convert the cis-diester 18 by a similar scheme to a derivative of tetraazabicyclooctane 6 was thwarted by an inversion of configuration that was introduced when treatment with hydrazine produced the dihydrazide 19 isolated in one isomeric form. The trans-stereochemistry of 19 was assigned on the basis of its relationship with 1,3-dinitroimidazolidine-4,5-dicarbamate 24. An absence of an AB quartet nmr signal for the C-2 methylene protons, a characteristic feature of cis-4,5-disubstituted imidazolidines,[11] shown by the cis-diester 23 and the cis-dicarboxylic acid 29, suggested the presence of 24 as the trans-isomer. Presumably the quartet pattern was masked in the spectra for the dinitrosamines 19 - 22. Diethyl 1,3-dinitroimidazolidine-4,5-dicarbamate 24 was shown to be the trans-isomer by an X-ray crystallographic analysis.[12]

$(CH_2)_n\ (CH(NH_2)CO_2R)_2$

7 $n = 1,\ R = CH_3$

8 $n = 0,\ R = CH_3,\ C_2H_5$



9 $X = NO,\ Y = CO_2CH_3$

10 $X = NO,\ Y = CONHNH_2$

11 $X = NO,\ Y = CON_3$

12 $X = NO,\ Y = NCO$

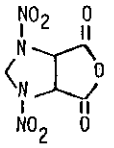
13 $X = NO,\ Y = NHCO_2C_2H_5$

14 $X = NO_2,\ Y = CO_2CH_3$

15 $X = NO_2,\ Y = CO_2H$

16 $X = NO_2,\ Y = NH_2$

17 $X = NO_2,\ Y = CONHNH_2$



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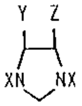


18 $X = NO,\ Y = Z = CO_2R$

19 $X = NO,\ Y = Z = CONHNH_2$

20 $X = NO,\ Y = Z = CON_3$

21 $X = NO,\ Y = Z = NCO$

22 $X = NO,\ Y = Z = NHCO_2C_2H_5$

23 $X = NO_2,\ Y = Z = CO_2R$

24 $X = NO_2,\ Y = Z = NHCO_2C_2H_5$

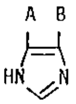
28 $X = NO_2,\ Y = CO_2H,\ Z = CO_2CH_3$

29 $X = NO_2,\ Y = Z = CO_2H$

31 $X = NO_2,\ Y = CO_2Sn(C_4H_9)_3,\ Z = CON_3$

32 $X = NO_2,\ Y = Z = CO_2Sn(C_4H_9)_3$

33 $X = NO,\ Y = Z = CONN{=}C(CH_3)_2$



25 $A = B = CO_2CH_3$

26 $A = B = CONHNH_2$

27 $A = CO_2H,\ B = CO_2CH_3$

This base catalyzed inversion was in agreement with an earlier report[13] that described an inversion that accompanied the conversion of a dialkyl *cis*-cyclopentane-1,2-dicarboxylate to the corresponding *trans*-dihydrazide in a reaction with hydrazine. A similar inversion occurred when treatment with hydrazine converted the *cis*-diester 9, after isolation from its *trans*-isomer by flash chromatography, to a dihydrazide 10 as a mixture of the *cis*- and *trans*- isomers.

In a straightforward manner the diazide 20 was obtained from the dihydrazide 19 and nitrous acid. Thermolysis of the diazide gave a bisisocyanate 21 since the product, without isolation, was converted to a dicarbamate 22 by treatment with ethanol. As expected for the *trans*-, but not the *cis*-, configuration there was an inability of the dicarbamate 22 to undergo an intramolecular ring closure to a derivative of tetraazabicyclooctane 6 in a reaction with formaldehyde or an equivalent reagent. In further indirect support for its *trans*-configuration the unisolated bisisocyanate 21 reacted with water to give an intractable mixture of unidentified material in which a cyclic urea was not detected. In reactions with nitric acid (100%) the dinitrosamines 18 and 22 gave the dinitramines 23 and 24. When treated with hydrazine the former unexpectedly underwent an elimination of nitrous acid to give dimethyl imidazole-4,5-dicarboxylate 25 and the corresponding dihydrazide 26. A similar elimination afforded monomethyl imidazole-4,5-dicarboxylate 27 when monomethyl 2,3-dinitroimidazolidine-4,5-dicarboxylate 28 was treated with triethylamine and diphenylphosphoryl azide. The monoester 28 was obtained from the diester 23 by straightforward hydrolysis to the dicarboxylic acid 29 and dehydration to 1,3-dinitroimidazolidine-4,5-dicarboxylic acid anhydride 30 that was then treated with methanol. Although tri-*n*-butyltin azide[14] converted phthalic anhydride via a Curtius rearrangement to isatoic anhydride the similar treatment of the anhydride 30 gave tri-*n*-butyltin *cis*-1,3-dinitro-4-azidocarbonylimidazolidine-5-carboxylate 31, an unstable salt that disproportionated to the bis-tri-*n*-butyltin salt 32 on treatment with either *t*-butanol or ethanol.

EXPERIMENTAL

Caution is recommended in handling azides, nitrosamines, and nitramines since they tend to be explosive and certain nitrosamines and nitramines were reported to be carcinogenic.

Instruments included Pye-Unicam SP-200 (ir), Varian A-60 and Joel Fx 90 Q (nmr) and HP 5790 (Gc/Ms). Elemental analyses were obtained from Micro-Tech. Lab., Skokie, Illinois and Midwest Micro Lab., Indianapolis, Indiana. Melting points were determined from a Thomas-Hoover mp apparatus and were uncorrected. *meso*-Dibromo-succinic acid and -glutaric acid were commercially available. Dimethyl diaminoglutarate 7 [15] and dimethyl *meso*-diaminosuccinate 8 [16] were prepared by reported procedures.

Dimethyl 1,3-dinitrosohexahydropyrimidine-4,6-dicarboxylate 9. The diamine 7 as its dihydrochloride salt (7.8 g, 0.03 mol) was dissolved in water (50 ml). To the stirred solution, formaldehyde (37%, 2.8 g, 0.035 mol) was slowly added and the stirring was continued at 25°C for 30 min. The mixture was cooled to 0°C, a solution of sodium nitrite (4.6 g, 0.066 mol) in water (10 ml) was added in one portion, stirred for 10 min at 0-5°C and extracted with ether. The extract was dried (Na_2SO_4) and the ether was removed to leave a yellow gum. Trituration with ether gave a waxy solid, (6.7 g, 88%), mp 93-100°C [which showed two closely moving spots on tlc (silica gel, chloroform)]. Silica gel chromatography (chloroform) separated two compounds. The *cis*-diester **9** was slightly predominant mp 112-115°C (dec), Ir (KBr): 1735, 1475, 1455, 1435 cm^{-1}. Nmr (acetone-d_6): δ 7.4 and 6.2 (2H, dd, J = 14 and 14 Hz, NCH_2N), 4.9 (2H, m, NCH), 3.7 (6H, m, CH_3), 2.6 (2H, m, CH_2). Anal. Calcd for $C_8H_{12}N_4O_6$: C, 36.92; H, 4.61; N, 21.54. Found: C, 36.57; H, 4.37; N, 21.30.

Dimethyl *cis*-1,3-dinitrohexahydropyrimidine-4,6-dicarboxylate 14. To nitric acid (100%, 15 ml) stirred at -45°C (dry ice in acetonitrile) the *cis*-dinitroso compound **9** (1.3 g, 0.005 mol) was slowly added. The dry ice bath was replaced by an ice bath. The reaction mixture was warmed to 0°C in 10 min and was poured onto crushed ice to bring about the separation of the *cis*-dinitrodiester **14** as a colorless solid (1.1 g, 78%) mp 102-104°C (dec) from a mixture of ether and pentane. Ir (KBr): 1730, 1550, 1530, 1300, 1285 cm^{-1}. Nmr ($CDCl_3$): δ 7.1 and 5.2 (2H, dd, J = 14 and 14 Hz, NCH_2N), 5.4 (2H, t, J = 5.5 Hz, NCH), 3.8 (6H, s, CH_3) 2.7 (2H, m, CH_2). Anal. Calcd for $C_8H_{12}N_4O_8$: C, 32.87; H, 4.11; N, 19.17. Found: C, 32.63; H, 4.05; N, 19.03.

***cis*-1,3-Dinitrohexahydropyrimidinedicarboxylic acid 15.** The dimethyl ester **14** (2.92 g, 0.01 mol) was suspended in concentrated hydrochloric acid (25 ml) and heated at 80-90°C for 1 h. The mixture was concentrated and residual water was removed azeotropically with benzene. The dicarboxylic acid **15** (2.1 g, 81%) was obtained as a colorless solid mp 210°C (dec) (chloroform). Ir (KBr): 3400-2900, 1755, 1720, 1555, 1525, 1355, 1305, 1295 cm^{-1}. Nmr (acetone-d_6): δ 9.3 (2H, s, OH), 7.2 (1H, d, J = 15 Hz, NCH_2N), 5.3 and 5.1 (2H, dd, J = 6.5 and 6.5 Hz, NCH), 5.2 (1H, d, J = 15 Hz, NCH_2N), 2.7 (2H, m, CH_2). Anal. Calcd for $C_6H_8N_4O_8$: C, 27.27; H, 3.03; N, 21.21. Found: C, 27.27; H, 3.00; N, 21.48.

***cis*-1,3-Dinitrosohexahydropyrimidine-4,6-dicarboxylic acid dihydrazide 10.** To a solution of a mixture of *cis*- and *trans*-dinitroso diester **9** (2.6 g, 0.01 mol) in methanol (50 ml) hydrazine hydrate (1.0 g, 0.02 mol) was added and the mixture was heated at 65°C for 4 h. On cooling the reaction mixture the *cis*-dihydrazide **10** was separated as a colorless solid, (1.7 g, 64%), mp 213-216°C (methanol). Ir (KBr): 3250, 1680, 1460 cm^{-1}. Nmr (DMSO-d_6): δ 7.4 and 6.2 (2H, dd, J = 14 and 14 Hz, NCH_2N), 4.3 (2H, m, NCH), 2.5 (2H, m, CH_2). ^{13}C Nmr (DMSO-d_6): 165.83, 62.52, 54.65, 27.34. Anal. Calcd for $C_6H_{12}N_8O_4$: C, 27.69; H, 4.62; N, 43.07. Found: C, 27.36; H, 4.83; N, 41.21.

The above reaction when repeated with the *cis*-diester **9** gave a mixture of of *cis*- and *trans*-dihydrazide in a ratio of 2:1.

***cis*-1,3-Dinitrosohexahydropyrimidine-4,6-dicarboxylic acid diazide 11.** To a suspension of the *cis*-hydrazide **10** (1.3 g, 0.005 mol) in tetrahydrofuran (10 ml) at -15°C (dry ice in carbon tetrachloride) hydrogen chloride in ether (∼ 7 M, 3.5 ml) was added followed by t-butyl nitrite (1.4 ml, 0.011 mol). The mixture was stirred for 30 min and poured onto crushed ice to isolate the cis-diazide 11 as a colorless solid (1.2 g, 88%) mp 98°C (dec) (chloroform). Elemental analysis was precluded by its instability. Ir (KBr): 2180, 1715, 1700, 1490, 1460 cm^{-1}. Nmr ($CDCl_3$/DMSO-d_6): δ 7.5 and 6.2 (2H, dd, J = 13 and 13 Hz, NCH_2N), 4.7 (2H, m, NCH), 2.6 (2H, m, CH_2).

Diethyl cis-1,3-dinitrosohexahydropyrimidine-4,6-biscarbamate 13. The cis-diazide 11 (1.4 g, 0.005 mol) in dry benzene (25 ml) was heated at 80°C for 30 min. The reaction was monitored (Ir) for the diminution in absorption by the azido group. After cooling, ethanol (2 ml) was added and the reaction mixture was stirred at room temperature overnight. Solvents were removed to leave the biscarbamate 13 as a pale yellow solid (1.1 g, 69%), mp 162°C (benzene). Ir (KBr): 3360, 1730, 1710 cm^{-1}. Nmr (acetone-d_6): δ 5.0-7.4 (4H, m, NCH_2N and NCH), 4.1 (4H, m, OCH_2), 2.9 (2H, m, CH_2), 1.2 (6H, t, J = 7 Hz, CH_3). Anal. Calcd for $C_9H_{16}N_6O_6$: C, 35.53; H, 5.26; N, 27.63. Found: C, 35.71; H, 5.24; N, 27.64.

6,8-Dinitroso-2,4,6,8-tetraaza[3.3.1]bicyclononan-3-one 5b. The diazide 11 (0.7 g, 2.5 mmol) was heated in dry benzene (10 ml) at 80°C for 30 min. After cooling, a solution of water (0.5 ml) in acetone (2 ml) was added as a copious evolution of gas was noted. The reaction mixture was stirred at room temperature overnight. Solvents were removed to leave the dinitroso compound 5b as a pale yellow solid (0.31 g, 61%), mp 175°C (dec) (acetone); ir (KBr): 3235, 1690, 1470 cm^{-1}. Nmr (DMSO-d_6): δ 8.0 (2H, br, NH), 6.3 (3H, m, NCH_2N and NCH), 4.3 (1H, d, J = 16 Hz, NCH_2N), 2.1 (2H, m, CH_2). ^{13}C (DMSO-d_6), 153.11, 152.65, 63.95, 59,79, 54.72, 53.94, 52.05, 46.33, 30.61, 28.64. Anal. Calcd for $C_5H_8N_6O_3$: C, 30.00; H, 4.00; N, 42.00. Found: C, 30.29; H, 4.21; N, 39.96.

6,8-Dinitro-2,4,6,8-tetraaza[3.3.1]bicyclononan-3-one 5c. To nitric acid (100%, 5 ml) at -45°C (dry ice in acetonitrile) the dinitroso compound 5b (0.5 g, 2.5 mmol) was slowly added with stirring. The reaction mixture was warmed to -5°C and poured onto crushed ice to isolate the dinitro compound 5c as a colorless solid (0.36 g, 62%), mp 190-193°C (dec) (acetone). Ir (KBr): 3360, 1740, 1695, 1540, 1380, 1310 cm^{-1}. Nmr ^{13}C (DMSO-d_6): δ 153.63, 61.61, 54.90, 26.56. Anal. Calcd for $C_5H_8N_6O_5$: C, 25.86; H, 3.45; N, 36.20. Found: C, 25.83; H, 3.46; N, 35.92.

Diethyl cis-1,3-dinitrosoimidazolidine-4,5-dicarboxylate 18 (R = C_2H_5). The diamino diester 8 (R = C_2H_5) (6.1 g, 0.03 mol) in water (50 ml) was treated with formaldehyde solution (37%, 2.8 g, 0.035 mol). The mixture was stirred at room temperature for 1 h, cooled to -5°C (ice-salt bath) and treated with sodium nitrite (4.6 g, 0.066 mol) followed by concentrated hydrochloric acid (10 ml). A yellow oil separated immediately. After stirring at 0°C for 30 min the mixture was extracted with ether. The extract was washed with saturated sodium bicarbonate solution and dried (Na_2SO_4). Evaporation gave the ester 18 (R = C_2H_5) as a viscous liquid. Flash chromatography (chloroform) from silica gel gave a light yellow solid, mp 55-62°C (ether and petroleum ether). Ir ($CHCl_3$): 1750, 1470 cm^{-1}. Nmr ($CDCl_3$): δ 7.2-5.1 (4H, m, NCH_2N and NCH) 4.2 (4H, m, OCH_2), 1.2 (6H, m, CH_3). Anal. Calcd for $C_9H_{14}N_4O_6$: C, 39.42; H, 5.11; N, 20.44. Found: C, 39.40; H, 5.13; N, 20.42. The dimethyl ester 18 (R = CH_3) (80%) was prepared in a similar manner, mp 90-94°C (ether). Ir (KBr): 1745, 1455, 1445 cm^{-1}. Nmr ($CDCl_3$): δ 5.0-7.1 (4H, m, NCH_2N and NCH) 3.9 and 3.8 (6H, 2s, OCH_3).

Diethyl cis-1,3-dinitroimidazolidine-4,5-dicarboxylate 23 (R = C_2H_5). Nitric acid (100%, 25 ml) was cooled to -45°C (dry ice in acetonitrile) and treated slowly with the dinitroso ester 18 (R = C_2H_5) (2.75 g, 0.01 mol). The reaction mixture was stirred for 20 min and poured onto crushed ice. The dinitro ester 23 (R = C_2H_5) was isolated as a colorless solid (2.4 g, 78%) and washed with ice water, mp 102-104°C (ether/petroluem ether). Ir ($CHCl_3$): 1760, 1570, 1280 cm^{-1}. Nmr ($CDCl_3$): δ 5.8 and 5.6 (2H, dd, J = 8 and 8 Hz, NCH_2N) 5.2 (2H, s, NCH), 4.3 (4H, q, J = 7 Hz, OCH_2), 1.3 (6H, t, J = 7 Hz, CH_3). Anal. Calcd for $C_9H_{14}N_4O_8$: C, 35.29; H, 4.58; N, 18.30. Found: C, 34.89; H, 4.63; N, 18.30. The dimethyl ester 23 (R = CH_3) (88%) was prepared similarly, mp 104-105°C (ether). Ir ($CHCl_3$): 1760, 1570, 1300; nmr ($CDCl_3$): δ 5.8 and 5.6 (2H, dd, J=8 and 8 Hz, NCH_2N), 5.2 (2H, s, NCH) 3.8 (6H, s, OCH_3).

cis-1,3-Dinitroimidazolidine-4,5-dicarboxylic acid 29. The dimethyl ester 23 (R = CH_3) (1.4 g, 0.005 mol) was suspended in concentrated hydrochloric acid (15 ml) and heated at 80-90°C for 2 h. The reaction mixture was concentrated and the last traces of water were removed azeotropically with benzene. The diacid 29 (0.8 g, 65%) was obtained as a colorless solid, mp 135°C (dec) (chloroform). Ir (KBr): 3350, 1775, 1745, 1560, 1535, 1300 cm^{-1}. Nmr (acetone-d_6): δ 10.7 (2H, s, OH); 5.8 and 5.5 (2H, dd, J = 7 and 7 Hz, NCH_2N), 5.4 (2H, s, NCH). Anal. Calcd for $C_5H_6N_4O_8$: C, 24.01; H, 2.42; N, 22.40. Found: C, 23.83; H, 2.42; N, 22.14.

Dimethy ester 25 and the dihydrazide 26 of imidazole-4,5-dicarboxylic acid. A mixture of the diester 23 (R = CH_3) (1.22 g, 0.005 mol) and hydrazine hydrate (0.5 g, 0.01 mol) was heated in ethanol (10 ml) at 80°C for 4 h. A colorless precipitate was isolated and washed with cold ethanol to give the diester 25, mp 205°C (ethanol) (lit.[10] mp 208°C). When the reaction was repeated with an excess of hydrazine hydrate the hydrazide 26 was obtained, mp >300°C (lit.[10] mp >400°C). Anal. Calcd for $C_5H_8N_6O_2$: C, 32.60; H, 4.35; N, 45.65. Found: C, 32.41; H, 4.32; N, 45.55.

1,3-Dinitroimidazolidine-4,5-dicarboxylic acid anhydride 30. The dicarboxylic acid 29 (2.5 g, 0.01 mol) was mixed with thionyl chloride (10 ml) and a drop of pyridine and heated at 40-50°C for 2 h. The anhydride 30 was obtained as a colorless solid in almost quantitative yield (2.2 g, 95%), mp 143°C (dec). Ir (KBr): 1890, 1805, 1550, 1320, 1290 cm^{-1}. Nmr (acetone-d_6): δ 6.6 and 5.6 (2H, dd, J = 10 and 10 Hz, NCH_2N) 6.3 (2H, s, NCH). The anhydride 30 was converted completely to the diacid 29 on storage with exposure to atmospheric moisture.

Tri-*n*-butyltin cis-1,3-dinitro-4-azidocarbonylimidazolidine-5-carboxylate 31. The anhydride 30 (1.2 g, 0.05 mol) was dissolved in dry dioxan (10 ml) and tri-*n*-butyltin azide (1.7 g, 0.05 mol) was added. The mixture was stirred at room temperature for 30 min. Solvent was removed to leave the tin salt 31 as a viscous liquid; a slow decomposition on storage at 25°C precluded elemental analysis. Ir ($CHCl_3$): 1740, 1690, 1560, 1285 cm^{-1}. Nmr ($CDCl_3$): δ 5.8 and 5.6 (2H, dd, J = 7 and 7 Hz, NCH_2N), 5.3 and 5.1 (2H, dd, J = 8 and 8 Hz, NCH), 0.7-2.0 (27H, m, butyl).

Bis-tri-*n*-butyltin *cis*-1,3-dinitroimidazolidine-4,5-dicarboxylate 32. The anhydride 30 (1.2 g, 0.05 mol) dissolved in dry dioxan (10 ml) was treated with tri-*n*-butyltin azide (1.7 g, 0.05 mol). The mixture was stirred at room temperature for 30 min. *t*-Butanol (5 ml) was added and the mixture was heated at 90-100°C for 2 h. Solvents were removed to leave the salt 32 as a colorless solid (1.8 g, 45%), mp 75-77°C. Ir ($CHCl_3$): 1690, 1555, 1290 cm^{-1}. Nmr ($CDCl_3$): δ 5.7 and 5.6 (2H, dd, J = 7 and 7 Hz, NCH_2N), 5.1 (2H, s, NCH) 0.7-1.9 (54H, m, butyl). Anal. Calcd for $C_{29}H_{58}N_4O_8Sn_2$: C, 42.08; H, 7.01; N, 6.77. Found: C, 42.08; H, 7.12; N, 6.72. The salt 32 was also obtained when compound 31 was treated with ethanol.

***cis*-1,3-Dinitro-4-methoxycarbonylimidazolidine-5-carboxylic acid 28.** The anhydride 30 (1.15 g, 5 mmol) was treated with methanol (10 ml) and stirred for 15 min at room temperature. Methanol was removed to leave the ester 28 as a colorless solid (1.32 g, 100%), mp 125-127°C (dec) (chloroform). Ir (KBr): 3500, 3200, 1760, 1735, 1555, 1320, 1295 cm^{-1}. Nmr (acetone-d_6): δ 9.1 (1H, s, OH), 5.8 and 5.6 (2H, dd, J = 7 and 7 Hz, NCH_2N), 5.5 (2H, s, NCH), 3.8 (3H, s, OCH_3). The ester 28 was converted to the known diacid 29 and diester 24 (R = CH_3).

The dihydrazide 19 of 1,3-dinitrosoimidazolidine-4,5-dicarboxylic acid. To a solution of the *cis*-dinitroso diester 18 (R = CH_3) (1.2 g, 5.0 mmol) in methanol (25 ml) hydrazine hydrate (0.5 g, 10 mmol) was added and the mixture was heated at 65°C for 4 h. Methanol was removed to give the dihydrazide 19 as a yellow gum (0.79 g, 66%), after trituration with ether. Treatment with acetone converted the dihydrazide 19 to a bishydrazone 33 of acetone, mp 222°C (dec) (acetone). Ir (KBr): 3260, 1705, 1680, 1460 cm^{-1}. Anal. Calcd for $C_{11}H_{18}N_8O_4$: C, 40.49; H, 5.52; N, 34.36. Found: C, 40.04; H, 5.61; N, 34.25.

1,3-Dinitrosoimidazolidine-4,5-dicarboxylic acid diazide 20. A suspension of the dihydrazide 19 (1.2 g, 5 mmol) in tetrahydrofuran (10 ml) was cooled to -15°C (dry ice in carbon tetrachloride). Hydrogen chloride in ether (7 M, 3.5 ml, 25 mmol) was added followed by *t*-butyl nitrite (1.4 ml, 11 mmol). The mixture was stirred at -15°C to -10°C for 30 min and poured onto crushed ice. The diazide 20 separated as a colorless solid (1.1 g, 83%), mp 90°C (dec) (chloroform). Its slow decomposition at room temperature precluded elemental analysis. Ir (KBr): 2180, 2130, 1690, 1445 cm^{-1}. Nmr ($CDCl_3$): δ 5.2-7.0 (m, *syn*- and *anti*- rotational isomers).

Diethyl 1,3-dinitrosoimidazolidine-4,5-biscarbamate 22. The diazide 20 (1.35 g, 5 mmol) was suspended in dry benzene (25 ml) and heated at 80°C for 30 min. The reaction was monitored by the diminution of azide ir absorption. Ethanol (2 ml) was added and the reaction mixture was stirred at room temperature overnight. Solvents were removed to leave the biscarbamate 22 as a light yellow solid (1.1 g, 74%), mp 158-160°C (benzene). Ir (KBr): 3270, 1690, 1460, 1450 cm^{-1}. Nmr (acetone-d_6): δ 7.9 (2H, br, NH) 6.5, 5.8 and 5.1 (4H, m, NCH_2N and NCH), 4.0 (4H, q, J = 7 Hz, OCH_2), 1.1 (6H, t, J = 7 Hz, CH_3); ^{13}C nmr (acetone-d_6): δ 156.35, 72.53, 67.06, 65.44, 62.06, 61.54, 14.58. Anal. Calcd for $C_9H_{16}N_6O_6$: C, 35.53; H, 5.26; N, 27.63. Found: C, 35.71; H, 5.24; N, 27.64.

Diethyl trans-1,3-dinitroimidazolidine-4,5-biscarbamate 24. The dinitrosobiscarbamate 22 (3.04 g, 0.01 mol) was slowly added to nitric acid (100%, 25 ml), cooled to -45°C (dry ice and acetonitrile). The dry ice bath was replaced by an ice-salt bath. The reaction mixture was warmed to 0°C in 15 min, poured onto crushed ice and extracted with ethyl acetate. The extract was dried (Na_2SO_4) and the solvent was removed to leave the dinitrobiscarbamate 24 (2.4 g, 72%), mp 190°C (dec) (benzene). Ir (KBr): 3280, 1680, 1520, 1280 cm^{-1}. Nmr (acetone-d_6): δ 7.5 (2H, br, NH), 5.8 (2H, m, NCH), 5.6 (2H, s, NCH_2N), 4.0 (4H, q, J = 7 Hz, OCH_2), 1.1 (6H, t, J = 7 Hz); ^{13}C (DMSO-d_6): δ 156.55, 74.02, 67.78, 61.12, 14.52. Anal. Calcd for $C_9H_{16}N_6O_8$: C, 32.14; H, 4.76; N, 25.00. Found: C, 31.92; H, 4.51; N, 24.98.

REFERENCES

1. George F. Wright, "Methods of Formation of the Nitramino Group, its Properties and Reactions," H. Feuer, ed., "The Chemistry of the Nitro and Nitroso Groups," S. Patai, Ser. ed., "The Chemistry of Functional Groups," John Wiley and Sons, New York, 1969, pp. 614-684.
2. L. Wenjie, H. Guifen, and C. Miaohong, Proceedings of the International Symposium on Pyrotechnics and Explosives, Oct. 12-15, 1987, Beijing, China. Academic Publishers. 1987, 187.
3. J. Boileau, J. M. L. Emeury, and J. P. A. Kehren, Ger. Offen. 2,435 651 [Chem. Abstr., 1975, 30483r].
4. W. M. Koppes, M. Chaykovsky, H. G. Adolph, R. Gilardi, and C. George, J. Org. Chem., 1987, 52, 1113.
5. A. T. Nielsen, "ONR Workshop on Crystalline Energetic Materials Synthesis," Nov. 3-5, 1986, Maryland. CPIA Publication 1987, 330.
6. i) R. F. Evans, Aust. J. Chem., 1967, 20, 1643; ii) J. H. Boyer and G. Kumar, Heterocycles, 1984, 22, 2351.
7. W. J. Schnabel and E. Kober, J. Org. Chem., 1969, 34, 1162.
8. R. G. Gafurov, E. M. Sogomonyan, and L. T. Eremenko, Izv. Akad. Nauk. SSSR. Ser. Khim., 1973, 12, 2826. Eng. 2764.
9. W. E. Bachmann, W. J. Horton, E. L. Jenner, N. W. MacNaughton, and C. E. Maxwell, J. Amer. Chem. Soc., 1950, 72, 3132.
10. T. Shiori, K. Ninomiya, and S. Yamada, J. Amer. Chem. Soc., 1972, 94, 6203.

11. P. Cerutti and H. Schmid, Helv. Chim. Acta, 1964, 47, 203.

12. Personal communication from Dr. E. D. Stevens who plans to publish elsewhere.

13. J. H. Muller, M. N. Donin, W. E. Behnke, and K. Hofmann, J. Amer. Chem. Soc., 1951, 73, 2487.

14. H. R. Kricheldorf, G. Schmarz, and T. Kaschig, Angew. Chem. Internat. Ed. Engl., 1977, 16, 550.

15. H. Newman, J. Heterocycl. Chem., 1974, 449.

16. P. W. Feit and O. T. Nielsen, J. Med. Chem., 1967, 10, 927.

17. R. N. Castle and W. S. Seese, J. Org. Chem., 1958, 23, 1534.

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