Substituent Effects in the Conversion of Azido- and Diazidotrinitrobenzenes to Benzofuroxans and Difuroxans

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The preparation of a number of substituted dinitrobenzofurazan oxides (dinitrobenzofuroxans) and nitrobenzobis(oxadiozoles) (nitrobenzodifuroxans), in which the substituents were amino, fluoro, formamido, hydroxy, and ureido groups, by thermolysis of azido precursors is described. The ease of thermolysis appears to be an inverse function of the angle of twist of the nitro groups *ortho* to the azido group from the plane of the benzene ring. Amino- and hydroxy-substituted dinitrobenzofuroxans and nitrobenzodifuroxans were found to be much more stable than their non-nitro-substituted counterparts.

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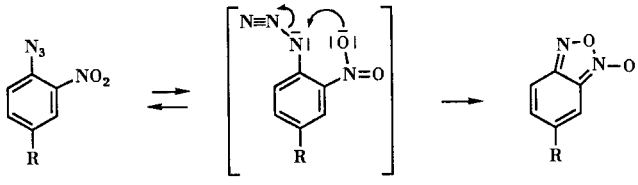
Introduction.

Thermolysis of 2-nitroaryl azides to benzofurazan oxides (benzofuroxans) is accelerated by electron-withdrawing substituents in the 4-position [1]. More extensive substitution appears to slow the reaction, judging from the thermolysis temperatures employed. In the case of 3 and 6 substituents, this may be due to steric interference with the planar, cyclic transition state (Scheme 1). In the series

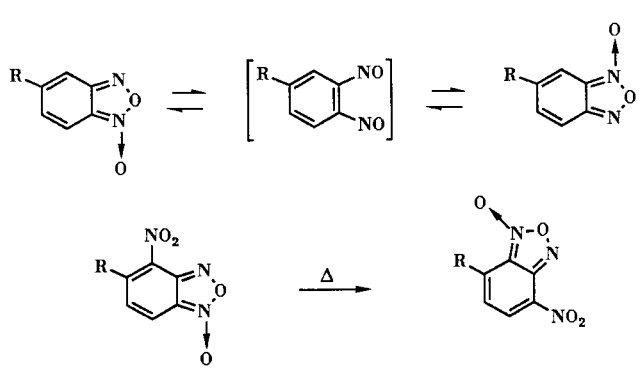
Scheme 1



2-nitrophenyl azide, 2,4-dinitrophenyl azide, 2,4,6-trinitrophenyl azide, the thermolysis rate first increases strongly and then appears to remain about the same.

In this paper, we describe the thermolysis, or, in some cases, attempted thermolysis of amino-, hydroxy-, and fluorine-substituted 2,4,6-trinitrophenyl azides and 2,4,6-trinitrophenylene diazides to the corresponding benzofuroxans and benzodifuroxans [benzobis(oxadiazoles)].

Scheme 2



When substituents are present in a benzofuroxan, it is sometimes difficult to determine the exact structure because certain benzofuroxans undergo rapid isomerization *via* a dinitroso intermediate (Scheme 2) [3]. Also, nitrobenzofuroxans undergo the Boulton-Katritzky rearrangement, in which isomers interconvert depending upon the temperature and solvent (Scheme 2) [2,4].

The benzofuroxans and benzodifuroxans described here were isolated as single products. There was no evidence for the existence of more than one isomer in each case. Structures were assigned to maximize hydrogen-bonding between amino or hydroxyl hydrogen and nitro and *N*-oxide groups, and to avoid electronic repulsion between nitro and *N*-oxide groups. All of the benzofuroxans are depicted as 5,7-dinitrofurazan 3-oxides. Steric factors must also play an important role in determining the actual structure of these products in the crystalline state and in solution. It is to be understood, therefore, that certain compounds with bulky substituents, (*e.g.* **3b**), may actually exist as the 1-oxide isomers in which steric crowding may be lessened.

Synthesis of Dinitrobenzofuroxans.

5-Fluorotrinitro-1,3-benzenediamine (**1a**, Scheme 3) reacted rapidly with sodium azide in acetonitrile-water to give, in high yield and purity, a yellow product which was found to be the benzofuroxan **3a** [5]. No trace of an azido group was seen in the infrared spectrum. This transformation, in which the intermediate azide **2a** spontaneously decomposes at room temperature to give the benzofuroxan, appears to be without precedent. It may be assumed that intramolecular hydrogen bonding in **2a** enforces a high degree of coplanarity of the nitro groups with the benzene ring, thus facilitating the formation of the cyclic transition state (Scheme 1) and expulsion of nitrogen from the azide group. Such planarity of nitro groups resulting from intramolecular hydrogen bonding has been demonstrated for diamino-1,3,5-trinitrobenzene [6], sym-tri-

aminotrinitrobenzene [7], and, to a lesser extent, for **1a** [8].

It is interesting that removal of only one amino group in **2a** leads to a stable azide which requires elevated temperature for conversion to the benzofuroxan **4** [9]. Presumably, there is a lesser degree of coplanarity of the nitro groups in this azide than in **2a**, just as the nitro groups in 2,4,6-trinitroaniline are less coplanar than those in 1,3-diamino-2,4,6-trinitrobenzene [10].

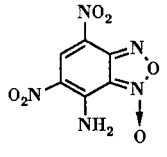
The benzofuroxan **3a** is very stable, at least in the solid state, in sharp contrast to the reported instability of 5-amino- and 5-hydroxybenzofuroxan [11]. This is probably also due to the presence of strong hydrogen-bonding between amino and nitro and/or *N*-oxide groups.

Scheme 3

1a-d **2a-d**

a R = NH_2
b R = $NHC(CH_3)_2$
c R = NHCHO
d R = F
e R = OH

3a-e



4

Another reaction sequence leading to **3a** begins with the di-*t*-butylamino derivative **1b**, which reacted with sodium azide in acetonitrile-water to give the stable azide **2b**. In this case, the bulky *t*-butyl groups undoubtedly disrupt hydrogen-bonding and twist the nitro groups out of the plane of the ring. Heating **2b** in refluxing toluene gave the benzofuroxan **3b**. Trifluoroacetic acid at room temperature solvolyzed both **2b** and **3b**, removing the *t*-butyl groups, to give **3a** in high yields.

Elevated temperature (refluxing tetrachloroethane) was also required for the conversion of the diformylamino azide **2c** to the benzofuroxan **3c**, despite the smaller N substituents. This further underscores the importance of nitro group conformation in the facile transformation **1a** → **3a**.

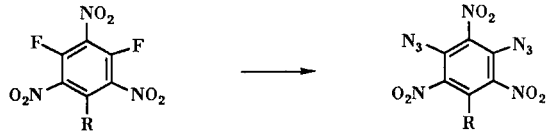
Careful addition of an equimolar amount of sodium azide to **1d** in toluene at room temperature gave mostly **2d**, which was not isolated, but converted directly to the benzofuroxan **3d** by refluxing the mixture. The crude **3d** contained impurities which could not be removed, in part due to the ease of hydrolysis of the fluorine substituents. It was hydrolyzed with formic acid to the dihydroxydinitrobenzofuroxan **3e**, which, because of its solubility in water, was readily separable from impurities. This compound is relatively unstable and frequently fumed off when heated in solvents above 80°. However, it is considerably more stable than simpler hydroxybenzofuroxans without nitro substituents [11].

Synthesis of Nitrobenzodifuroxans.

Difluoropicramide (**5a**, Scheme 4) reacted with sodium azide in acetonitrile-water to give the stable diazide **6a**. Spontaneous expulsion of nitrogen as in **2a** did also not occur in this case. Elevated temperature (refluxing toluene) was necessary to convert **6a** into the benzodifuroxan **7a**. An X-ray crystallographic structure determination showed that **7a** is the 4-amino isomer [12].

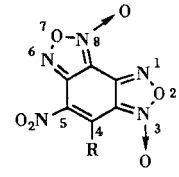
In a similar manner, the formamido and ureido substituted difluorides **5b** and **5c** were converted into the diazides **6b** and **6c**, and these were thermolyzed in inert solvents into the benzodifuroxans **7b** and **7c**.

Scheme 4



5a-d **6a-d**

a R = NH_2
b R = NHCHO
c R = $NHCONH_2$
d R = OH



7a-d

The formamido and ureido groups in **7b** and **7c** are unstable under solvolytic conditions. Thermolysis of **6c** in refluxing acetic acid resulted in removal of the carbamoyl function to give benzodifuroxan **7a**, and hydrolysis of both **7b** and **7c** in hot water also gave **7a**.

Difluoropicric Acid, **5d** [13], reacted with sodium azide in acetonitrile-water to give the diazide **6d**. Attempts to convert **6d** into the hydroxy-substituted benzodifuroxan

7d in refluxing benzene or toluene led only to the production of polymeric material and dark oils. It appears that **7d**, like **3e**, may be unstable to heat and decomposes under the conditions of the thermolysis of **6d**.

Summary and Conclusions.

This work has shown that amino- and amido-substituted dinitrobenzofuroxans and nitrobenzodifuroxans are readily prepared by thermolysis of azide precursors, generally under standard thermolysis conditions (110-150°). An exception is the diaminodinitrobenzofuroxan **3a**, whose azide precursor **2a** decomposes to **3a** at room temperature or below. The presumed reason for this anomaly is a high degree of planarity of the azide **2a**, due to intramolecular hydrogen-bonding, which would facilitate nitrogen expulsion *via* a cyclic, planar transition state.

The amino- and ureidonitro compounds are thermally stable as evidenced by their high melting points: **3a**, 291°; **7a**, 193°; **7c**, 193°. The formamido compounds **3c** and **7b** decompose at somewhat lower temperatures (melting points near 160°), while the hydroxynitrobenzofuroxan **3e** is much less stable (mp 106° with violent decomposition) and would probably not survive thermolysis of the azide precursor. This was also shown to be the case for the hydroxynitrobenzodifuroxan **7d**, whose synthesis from the azide precursor **6d** was attempted but failed.

EXPERIMENTAL

CAUTION: Many of the fluoro and azido compounds and benzofuroxans described here are explosives of varying sensitivity and should only be handled with appropriate precautions. Infrared (ir) spectra were taken on a Perkin-Elmer Model 283 recording spectrophotometer. ^{1}H nmr and ^{13}C nmr spectra were recorded on a Varian XL-200 instrument (TMS-referenced). Mass spectra were determined using a Finnigan Model 4000, GC EI-CI instrument. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. Melting points were determined on a Thomas-Hoover capillary apparatus and are uncorrected. All temperatures are in °C. The synthesis of the starting materials **1a-d** and **5a-d** is described in reference [14].

5,7-Dinitro-4,6-benzofurazandiamine 3-Oxide (**3a**).

To a stirred suspension of **1a** (1.044 g, 4 mmoles) in acetonitrile (60 ml) and water (30 ml) at room temperature was added sodium azide (780 mg, 12 mmoles). Complete solution occurred and, after several minutes, a yellow solid precipitated. After stirring for 2 hours, water (100 ml) was added, and the solid was filtered and dried to yield **3a** (900 mg, 88%), mp 292° dec. The analytical sample of the same mp was obtained by recrystallization from nitromethane; ir (potassium bromide): 3400, 3290, 1630, 1610, 1300, 1255, and 1215 cm^{-1}; ms: (CI, CH_4) m/z 67 (100), 257 (M+1, 21.2), 258 (3.1), 259 (4.4), 285 (M+29, 1.6), 297 (M+41, 1.0); ^{1}H nmr (DMSO-d_6): δ 10.04 (s, 2, NH_2), 10.87 (s, 2, NH_2); ^{13}C nmr (DMSO-d_6): δ 105.6, 106.8, 115.2, 143.9, 146.8, 150.4.

Anal. Calcd. for $C_6H_4N_6O_6$: C, 28.13; H, 1.57; N, 32.81. Found: C, 28.08; H, 1.56; N, 32.70.

1-Azido-3,5-di-*tert*-butylaminotrinitrobenzene (**2b**).

To a stirred solution of **1b** (747 mg, 2 mmoles) in acetonitrile (20 ml) at room temperature was added water (10 ml), followed immediately by sodium azide (390 mg, 6 mmoles). After 15 minutes, water (15 ml) was added slowly to the mixture and the yellow precipitate was filtered, washed with water, and dried over phosphorus pentoxide at room temperature to yield **2b** (720 mg, 91%). This compound decomposes at 160-165°; ir (potassium bromide): 3370, 2970, 2230 (sh) and 2140 (N_3), 1580, 1535 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.16 (s, 18, CH_3), 4.51 (s, 2, NH).

Anal. Calcd. for $C_{14}H_{20}N_8O_6$: C, 42.42; H, 5.09; N, 28.27. Found: C, 42.31; H, 5.00; N, 28.17.

N,N'-Di-*tert*-butyl-5,7-dinitro-4,6-benzofurazandiamine 3-Oxide (**3b**).

A solution of **2b** (396 mg, 1 mmole) in toluene (5 ml) was refluxed for 30 minutes, then cooled to 80° and hexane (10 ml) was added. After cooling to room temperature, the precipitate was filtered to yield **3b** (340 mg, 92%) as a salmon-colored solid, mp 165-167° dec. Recrystallization from toluene-hexane gave the analytical sample, mp 173-174° dec; ^{1}H nmr (deuteriochloroform): δ 1.36 (s, 9, CH_3), 1.69 (s, 9, CH_3), 9.32 (s, 1, NH), 9.96 (s, 1, NH).

Anal. Calcd. for $C_{14}H_{20}N_6O_6$: C, 45.65; H, 5.47; N, 22.82. Found: C, 45.59; H, 5.43; N, 22.78.

5,7-Dinitro-4,6-benzofurazandiamine 3-Oxide (**3a**) from **2b** and **3b**.

A mixture of **2b** (198 mg, 0.5 mmole) and trifluoroacetic acid (3 ml) was stirred at room temperature for 5 hours. Hexane (10 ml) was then added, and the yellow solid was filtered to give **3a** (110 mg, 86%), mp 292° dec, identified by ir, nmr and tlc.

In a similar manner, **3b** was converted by trifluoroacetic acid into **3a** in 80% yield.

1-Azido-3,5-diformamidotrinitrobenzene (**2c**).

To a stirred solution of **1c** (317 mg, 1 mmole) in acetonitrile (10 ml) and water (5 ml) at room temperature was added sodium azide (195 mg, 3 mmoles). After 30 minutes the solution was evaporated under reduced pressure to about 7 ml and water (10 ml) was added. The precipitated yellow solid was filtered to give **2c** (210 mg, 62%), mp 169-170° dec. Recrystallization from acetonitrile/water gave yellow crystals of the same mp; ir (potassium bromide): 2240 (sh) and 2155 (N_3), 1695, 1662, 1595, 1545 cm^{-1}.

Anal. Calcd. for $C_8H_4N_8O_8$: C, 28.24; H, 1.19; N, 32.94. Found: C, 28.32; H, 1.21; N, 32.79.

N,N'-Diformyl-5,7-dinitro-4,6-benzofurazandiamine 3-Oxide (**3c**).

A mixture of **2c** (34 mg, 0.1 mmole) and 1,1,2,2-tetrachloroethane (5 ml) was heated at reflux for 30 minutes, then cooled overnight in a refrigerator and filtered to yield **3c** (20 mg, 64%), mp 159-162° dec. Recrystallization from tetrachloroethane gave orange crystals, mp 162-163° dec; ir (potassium bromide): 1710, 1625, 1540, 1500, 1460, and 1342 cm^{-1}; ms: (CI, CH_4) m/z 67 (100), 257 (M+1-2CO, 4.4); ^{1}H nmr (acetone-d_6): δ 8.46 (s, 1, CH), 8.56 (s, 1, CH), 10.32 (br s, 2, NH).

Anal. Calcd. for $C_8H_4N_6O_8$: C, 30.78; H, 1.29; N, 26.93. Found: C, 30.68; H, 1.29; N, 26.76.

4,6-Difluoro-5,7-dinitrobenzofurazan 3-Oxide (**3d**).

To a stirred solution of **1d** (5.34 g, 20 mmoles) in toluene (250

ml) at room temperature was added powdered sodium azide (1.30 g, 20 mmoles) in portions over a period of 1 hour. After stirring for an additional hour, the mixture was refluxed for 1 hour, cooled and filtered, and the filtrate was then evaporated to dryness under vacuum. The residue was triturated with isopropyl ether (50 ml) and filtered to yield crude **3d** (4.28 g, 82%), mp 146-150° dec. Recrystallization from dichloromethane-hexane gave yellow prisms, mp 151-152° dec. A satisfactory chemical analysis could not be obtained for **3d** because of its contamination with complexing impurities which could not be removed by fractional crystallization. Column chromatography on silica gel, using various eluents, resulted in complete decomposition of **3d** to dark oils. The major impurity (about 10%) was isolated by hydrolysis of crude **3d** in refluxing water for 1 hour, filtering the insoluble solids, and recrystallizing from benzene. Obtained was a white solid, mp 195° dec, which was identified as benzotrifuroxan by comparison with an authentic sample, and by elemental analysis.

Anal. Calcd. for $C_6F_2N_4O_6$: C, 27.49; H, 0; N, 21.38; F, 14.50. Found: C, 27.55; H, <0.05; N, 22.47; F, 11.71.

N,N'-Di-*tert*-butyl-5,7-dinitro-4,6-benzofurazandiamine 3-Oxide (**3b**) from **3d**.

To a stirred solution of **3d** (262 mg, 10 mmoles) in toluene (20 ml) at room temperature a solution of 2-amino-2-methylpropane (366 mg, 50 mmoles) in toluene (10 ml) was added dropwise over a period of 5 minutes. After an additional 30 minutes the solution was washed with water (3 x 10 ml), then with saturated aqueous salt solution, dried (sodium sulfate) and evaporated under vacuum. The residue was triturated with isopropyl ether and filtered to give a salmon-colored solid which was identified (ir, nmr) as crude **3b** (275 mg, 75%): mp 160-165° dec. Recrystallization from toluene-hexane gave the pure sample, mp 173-174° dec.

5,7-Dinitro-4,6-benzofurazandiol 3-Oxide (**3e**).

A solution of **3d** (1.31 g, 5 mmoles) in 98% formic acid (10 ml) was stirred at room temperature for 2 hours after an initial exothermic reaction subsided. The solution was evaporated to dryness under vacuum at 50°, methanol (20 ml) was added, and this was evaporated again under vacuum. The residue was stirred with water (20 ml) and then filtered to remove some insoluble material. The deep red filtrate was evaporated under vacuum at 50° to leave a yellow solid which was dissolved in ethanol (20 ml) and evaporated again. This residue was triturated with 1:1 benzene:hexane (20 ml) and filtered to yield **3e** (850 mg, 66%) as a yellow solid, mp 106°, violent dec. The analytical sample was obtained from dichloromethane-hexane; ^{13}C nmr (DMSO-d_6): δ 104.5, 107, 126, 146, 158.5, 160.

Anal. Calcd. for $C_6H_2N_4O_8$: C, 27.92; H, 0.78; N, 21.71. Found: C, 27.84; H, 0.85; N, 21.65.

5,7-Dinitro-4-benzofurazanamine 3-Oxide (**4**).

To a suspension of 2,3,4,6-tetranitroaniline (3.28 g, 12 mmoles) in toluene (250 ml) was added a solution of sodium azide (1.56 g, 24 mmoles) in water (50 ml). The mixture was stirred vigorously for 2 hours during which time the solid dissolved. The toluene layer was separated, dried over magnesium sulfate, and filtered. The yellow solution was then heated with stirring at reflux for 30 minutes, cooled in a refrigerator for several hours, and filtered to yield 2.40 g (83%) of **4**, mp 269-270° dec. Recrystallization from acetonitrile/water gave orange plates of the same mp; ms: (CI, CH_4) m/z 242 (M + 1, 100), 243 (10.8), 244 (37.6), 270 (M + C_2H_5, 10.8), 282 (M + C_3H_5, 4.8).

Anal. Calcd. for $C_6H_3N_5O_6$: C, 29.89; H, 1.25; N, 29.05. Found: C, 29.95; H, 1.25; N, 29.03.

3,5-Diazidotrinitroaniline (**6a**).

To a solution of **5a** (1.32 g, 5 mmoles) in acetonitrile (45 ml) was added water (21 ml), followed immediately by sodium azide (975 mg, 15 mmoles). The solution was stirred at room temperature for 1 hour during which time a precipitate appeared. Water (60 ml) was then added slowly, followed by cooling the mixture in ice. The solid was filtered, washed with water, and dried at room temperature under vacuum to give **6a** (1.38 g, 89%) as yellow needles, mp 127°, violent dec; ir (potassium bromide): 2225 (sh) and 2160 cm^{-1} (N_3).

Anal. Calcd. for $C_6H_2N_{10}O_6$: C, 23.23; H, 0.65; N, 45.16. Found: C, 22.99; H, 0.70; N, 44.88.

4-Amino-5-nitrobenzo[1,2-*c*:3,4-*c'*]bis[1,2,5]oxadiazole 3,8-Dioxide (**7a**).

A mixture of **6a** (2.41 g, 7.77 mmoles) with toluene (80 ml) was refluxed for 30 minutes then cooled to 80° and hexane (60 ml) was added slowly. The mixture was cooled to room temperature and the solid filtered to yield **7a** (1.93 g, 98%), mp 192-193° dec. Recrystallization from acetonitrile gave yellow needles, mp 193° dec; ir (potassium bromide): 3400, 3290, 1660, 1635, 1580 cm^{-1}; ^{13}C nmr (DMSO-d_6): δ 101.2, 107.3, 110.5, 140, 142, 147.6.

Anal. Calcd. for $C_6H_2N_6O_6$: C, 28.36; H, 0.79; N, 33.07. Found: C, 28.31; H, 0.83; N, 32.90.

1,3-Diazido-5-formamidotrinitrobenzene (**6b**).

To a stirred solution of **5b** (1.46 g, 5 mmoles) in acetonitrile (40 ml) was added water (20 ml), followed immediately by sodium azide (975 mg, 15 mmoles). After 30 minutes the solution was concentrated under reduced pressure to 30 ml, and water (30 ml) was added. The precipitated solid was filtered to give **6b** (1.52 g, 90%), mp 132-133° dec. Recrystallization from acetone-water gave yellow plates, mp 134-135° dec; ir (potassium bromide): 2240 (sh) and 2140 (N_3), 1718 (sh), 1690, 1590, 1545 cm^{-1}.

Anal. Calcd. for $C_7H_2N_{10}O_7$: C, 24.86; H, 0.60; N, 41.42. Found: C, 24.93; H, 0.75; N, 40.34.

4-Formamido-5-nitrobenzo[1,2-*c*:3,4-*c'*]bis[1,2,5]oxadiazole 3,8-Dioxide (**7b**).

A mixture of **6b** (3.2 g, 9.47 mmoles) and toluene (125 ml) was refluxed for 30 minutes, filtered while still hot, then cooled, and the precipitated solid filtered. A second crop of solid was obtained by evaporating the filtrate to 25 ml. The combined solids were then dried at 105° for 2 hours. There was obtained 2.1 g (78%) of **7b**, mp 187-189° dec. Recrystallization from toluene gave orange crystals, mp 190-191° dec; ir (potassium bromide): 1700, 1620, 1580, 1525 cm^{-1}; ^{13}C nmr (DMSO-d_6): δ 100, 100.4, 125.6, 127.6, 145.6, 147.6, 160.6.

Anal. Calcd. for $C_7H_2N_6O_7$: C, 29.80; H, 0.71; N, 29.80. Found: C, 29.72; H, 0.73; N, 29.65.

3,5-Diazidotrinitrophenylurea (**6c**).

To a solution of **5c** (1.54 g, 5 mmoles) in acetonitrile (40 ml) was added water (20 ml), followed immediately by sodium azide (975 mg, 15 mmoles). The solution was stirred at room temperature for 1 hour and then evaporated under vacuum at 40° to 30 ml. Water (50 ml) was added slowly and the solid was filtered,

washed with water and dried over phosphorus pentoxide to yield **6c** (1.64 g, 93%); mp 152° dec. Recrystallization from acetonitrile-water gave pale yellow needles, mp 156° dec; ir (potassium bromide): 2210 (sh) and 2150 (N_3), 1730 cm^{-1} (CO).

Anal. Calcd. for $C_7H_3N_{11}O_7$: C, 23.80; H, 0.86; N, 43.63. Found: C, 23.80; H, 0.91; N, 43.53.

5-Nitro-4-ureidobenzo[1,2-*c*:3,4-*c'*]bis[1,2,5]oxadiazole 3,8-Dioxide (**7c**).

A suspension of **6c** (353 mg, 1 mmole) in chlorobenzene (20 ml) was refluxed for 30 minutes. The diazide dissolved in the hot solvent, and a solid then precipitated. The mixture was cooled and filtered to yield **7c** (260 mg, 88%); mp 190° dec. Recrystallization from tetrahydrofuran-hexane (charcoal) gave yellow crystals, mp 193° dec; ir (potassium bromide): 1730 (CO), 1670, 1640 cm^{-1}; ^{13}C nmr (DMSO-d_6): δ 102, 108, 122, 130.5, 140, 147, 151.5.

Anal. Calcd. for $C_7H_3N_7O_7$: C, 28.29; H, 1.02; N, 33.00. Found: C, 28.40; H, 1.13; N, 32.91.

Thermolysis of **6c** to **6a** in Acetic Acid.

A mixture of **6c** (353 mg, 1 mmole) in glacial acetic acid (15 ml) was refluxed for 1 hour, cooled, and filtered to yield a yellow solid (130 mg, 51%), mp 192° dec, which was identified as **6a** by ir and tlc.

Hydrolysis of **7b** and **7c** to **7a**.

A mixture of **7b** (56 mg, 0.2 mmole) and water (10 ml) was refluxed for 10 minutes. The cooled mixture was filtered to give **7a** (45 mg, 88%), identified by ir and tlc (silica gel, 20% acetonitrile-benzene). Similarly, a mixture of **7c** and water was refluxed for 30 minutes to give a 51% yield of **7a**.

3,5-Diazidopicric Acid (**6d**).

To a solution of **5d** (1.325 g, 5 mmoles) in acetonitrile (30 ml) was added water (15 ml), followed immediately by sodium azide (975 mg, 15 mmoles). The orange solution was stirred at room temperature for 1 hour and then concentrated under vacuum at 35° to 10 ml. Slow addition of 2*N* hydrochloric acid (10 ml) precipitated yellow needles which were filtered, washed with 2*N* hydrochloric acid, and dried over phosphorus pentoxide to give **6d** (1.3 g, 84%), mp 109° dec; ir (potassium bromide): 2220 (sh) and 2160 (N_3), 1610, 1575, 1555, and 1530 cm^{-1}.

Anal. Calcd. for $C_6H_1N_9O_7$: C, 23.16; H, 0.32; N, 40.52. Found: C, 23.17; H, 0.40; N, 40.43.

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