# Heterocyclic Compounds. XVI (1). Chemistry of the 1,4,2,3,5,6-Dithiatetrazine Ring System

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Derivatives of 1,4,2,3,5,6-dithiatetrazine-2,3,5,6-tetracarboxylate 1,4-dioxide can be made by reacting 1,2-dialkyl hydrazinodicarboxylates with thionyl chloride.

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In continuation of a study on the 1,4,2,3,5,6-dithiatetrazine ring system (2), we describe here several additional derivatives, as well as some attempted reactions. Treatment of 1,2-di-*i*-propyl hydrazinodicarboxylate (Id) and sulfur dichloride with triethyl amine gave tetra-*i*-propyl 1,4,2,3,5,6-dithiatetrazine-2,3,5,6-tetracarboxylate (IId). The conversions of 1,2-dimethyl hydrazinodicarboxylate (Ia), 1,2-bis(trichloroethyl) hydrazinodicarboxylate (Ic), and 1,2-di-*i*-butyl hydrazinodicarboxylate (Ie) to the corresponding dithiatetrazines (IIa, c, and e) were attempted, but failed in all cases. Previously, tetraethyl 1,4,2,3,5,6-dithiatetrazine-2,3,5,6-tetracarboxylate (IIb) had been oxidized by *m*-chloroperbenzoic acid to yield tetraethyl 1,4,2,3,5,6-dithiatetrazine-2,3,5,6-tetracarboxylate 1,4-dioxide (IIIb) (2). A similar oxidation of the di-*t*-butyl derivative (IIf) formed the corresponding di-*t*-butyl 1,4-dioxide (IIIf). However, IId decomposed under the same conditions to return the starting hydrazine Id.

It should be recalled that in the original work the 1,4-dioxide assignment was based on spectral arguments and known peracid chemistry. At this point, complete support for the 1,4-dioxide formulation, rather than an alternative 1,2-dioxide structure, came from the development of a new synthetic route. If the hydrazinodicarboxylates (Ib-f) were stirred with thionyl chloride, then the tetraalkyl dithiatetrazine tetracarboxylate 1,4-dioxides (IIIb-f) could be obtained directly in modest yield. The physical and spectral properties of compounds IIIb and IIIf prepared by the older two step procedure were identical to those seen for the same compounds in the one step preparation. It should be noted that this result lends welcomed support to the correct formulation of the dithiatetrazine ring system. Unfortunately, Ia and Ig did not react under these modified conditions, which is in keeping with their previous behavior.

Attempts to further oxidize the 1,4-dioxides to 1,1',4,4'-tetraoxides using hydrogen peroxide (3), "purple benzene" (4), and silver nitrate-benzoyl peroxide (5) met with failure or ruptured the ring to afford hydrazine salts. The replacement of thionyl chloride by sulfuryl chloride did not lead to any positive results, as the starting hydrazinodicarboxylates were generally recovered. Finally, cleavage of the carbamate side chains under basic (1), acidic (6-8), or neutral (9) conditions in all cases resulted in a degradation of the dithiatetrazine ring to hydrazine salts and sulfur.

Compounds Ic and IIIc were submitted for herbicidal and insecticidal screening (PPE Industries, Inc., Barberton, Ohio). In pre-emergence tests, good activity was seen against *Digitaria sanguinalis, Echinochloa crusgalli, Sesbania* ssp., *Sida spinosa,* and *Sorghum halepense*; however, these results were not confirmed by later post-emergence assays.

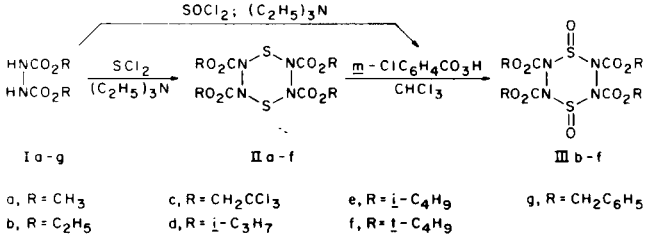


Table I

Tetraalkyl 1,4,2,3,5,6-Dithiatetrazine-2,3,5,6-tetracarboxylate 1,4-Dioxides

| Compound No. | M.p. °C | Yield % | Molecular Formula | Analysis % (a) Calcd. C | H | N | S | Found C | H | N | S |
|---|---|---|---|---|---|---|---|---|---|---|---|
| IIIb | 177-179 | 15 | $C_{12}H_{20}N_4O_{10}S_2$ | 32.43 | 4.54 | 12.60 | 14.43 | 32.12 | 4.46 | 12.61 | 14.43 |
| IIIc | 228-229 | 35 | $C_{12}H_8Cl_{12}N_4O_{10}S_2$ | 16.78 | 0.93 | 6.53 | 7.46 | 16.29 | 0.92 | 6.14 | 7.03 |
| IIId | 188-190 | 20 | $C_{16}H_{28}N_4O_{10}S_2$ | 38.40 | 5.60 | 11.20 | 12.80 | 38.71 | 5.66 | — | — |
| IIIe | 163-164 | 10 | $C_{20}H_{36}N_4O_{10}S_2$ | 43.17 | 6.47 | 10.07 | 11.51 | 43.16 | 6.63 | 10.21 | 11.10 |
| IIIf | 187-188 | 30 | $C_{20}H_{36}N_4O_{10}S_2$ | 43.17 | 6.47 | 10.07 | 11.51 | 43.05 | 6.65 | 9.89 | 11.79 |

(a) IIIc: Calcd. Cl, 49.65; Found Cl, 49.74.

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Table II

Spectral Data for the Tetraalkyl 1,4,2,3,5,6-Dithiatetraazine-2,3,5,6-tetracarboxylate 1,4-Dioxides

| Compound | Nuclear Magnetic Resonance | Infrared |
|---|---|---|
| IIIb | 1.36 (12H, t) and 4.43 (8H, q) (a) | 2995 (C-H), 1770 (C=O), 1460, 1370 ($CH_3$), 1255 (C-O), 1190 (S=O), 742 and 725 (N-S) |
| IIIc | 4.8 (s) | 2960 (C-H), 1782, 1745 (C=O), 1275 (C-O), 1195 (S=O), 1110 (C-N), 810 (C-Cl), and 760 (N-S) |
| IIId | 1.33 (24H, d), and 5.15 (4H, septet) (a) | 2920 (C-H), 1738 (C=O), 1460 ($CH_3$), 1272 (C-O), 1185 (S=O), 1100 (C-N), and 750 (N-S) |
| IIIe | 0.93 (24H, d), 1.9 (4H, multiplet), and 4.1 (8H, d) | 3000 (C-H), 1790, 1765 (C=O), 1400 ($CH_3$), 1300 (C-O), 1200 (S=O), 1100 (C-N), and 760 (N-S) |
| IIIf | 1.51 (s) | 2995 (C-H), 1765, 1755 (C=O), 1450 ($CH_3$), 1395, 1370 ($t$-$C_4H_9$), 1290 (C-O), 1185 (S=O), and 740 (N-S) |

(a) Hexadeuterioacetone was the solvent.

## EXPERIMENTAL

Melting points were determined on a Reichert Thermopan apparatus and were not corrected. Microanalyses were provided by Chemalytics, Inc., Tempe, Arizona. Infrared spectra were in potassium bromide using a Perkin-Elmer 257 spectrometer. Proton nuclear magnetic resonance spectra were obtained on a Varian EM-360 spectrometer with deuteriochloroform as the solvent unless otherwise stated with tetramethylsilane as the internal reference. The progress of all reactions and the purity of the products were followed by silica gel (GF-254) thin layer chromatography with iodine vapor or ultraviolet light for detection purposes.

Tetra-*i*-propyl 1,4,2,3,5,6-Dithiatetrazine-2,3,5,6-tetracarboxylate (IId).

Triethylamine (5.6 ml., 0.040 mole) in dry ether (300 ml.) was added dropwise with stirring over a 3.5 hour period to a solution of 1,2-di-*i*-propyl hydrazinodicarboxylate (4.1 g., 0.020 mole) and sulfur dichloride (1.3 ml., 0.020 mole) in dry ether (700 ml.). After filtration of the amine salt, the solvent was evaporated to dryness under reduced pressure. The residue was crystallized from methanol to give tetra-*i*-propyl 1,4,2,3,5,6-dithiatetrazine-2,3,5,6-tetracarboxylate (0.94 g., 20%), m.p. 152-153°; ir: 2920 (C-H), 1738 (C=O), 1460 ($CH_3$), 1272 (C-O), 1100 (C-N), and 750 (N-S) $cm^{-1}$; nmr (hexadeuterioacetone): $\delta$ 1.32 (24 H, d, 6 Hz) and 5.06 (4 H, septet, 6 Hz).

*Anal.* Calcd. for $C_{16}H_{28}N_4O_8S_2$: C, 41.02; H, 5.98; N, 11.97; S, 13.68. Found: C, 40.84; H, 5.64; N, 11.80; S, 13.62.

Tetra-*t*-butyl 1,4,2,3,5,6-Dithiatetrazine-2,3,5,6-tetracarboxylate 1,4-Dioxide (IIf).

A solution of tetra-*t*-butyl 1,4,2,3,5,6-dithiatetrazine-2,3,5,6-tetracarboxylate (0.5 g., 0.001 mole) and *m*-chloroperbenzoic acid (0.7 g., 0.004 mole) in chloroform (50 ml.) was refluxed for 24 hours. The solution was extracted with saturated aqueous sodium bicarbonate (2 x 50 ml.), dried over sodium sulfate, and evaporated *in vacuo* to give a yellow oil. This residue was dissolved in methanol and on standing deposited white crystals of the desired tetra-*t*-butyl 1,4,2,3,5,6-dithiatetrazine-2,3,5,6-tetracarboxylate 1,4-dioxide (0.2 g., 35%), m.p. 187-188°. The spectral and physical properties were identical to a sample prepared by the thionyl chloride route (see below).

Tetraalkyl 1,4,2,3,5,6-Dithiatetrazine-2,3,5,6-tetracarboxylate 1,4-Dioxides (IIIb-f).

Triethylamine (5.6 ml., 0.040 mole) in dry ether (300 ml.) was added dropwise with stirring over a 3.5 hour period to a solution of an appropriate 1,2-dialkyl hydrazinodicarboxylate (0.020 mole) and thionyl chloride (1.7 ml., 0.020 mole) in dry ether (700 ml.). After filtration of the amine salt, the solvent was evaporated to dryness under reduced pressure. The residue was recrystallized from methanol in the case of both IIIb and IIIf, while carbon tetrachloride was used for IIIc and acetonitrile-water for IIIe. Compound IIId was purified by sublimation (see Tables I and II).

## REFERENCES AND NOTES

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