Heterocyclic Compounds. XIII (1). Synthesis of the 1,4,2,3,5,6-Dithiatetrazine Ring System

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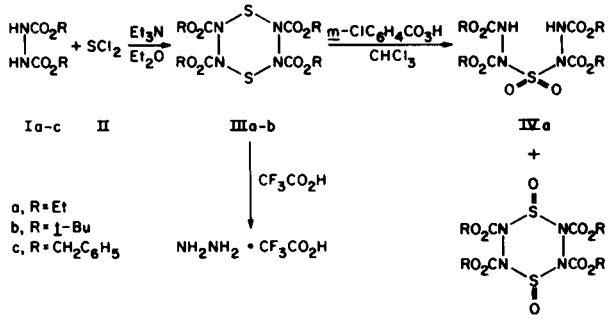
Sir:

Six-membered rings containing four nitrogen atoms and two other identical nuclei, located 1,4 to each other, are known for boron, silicon, and phosphorus (2-4). No examples have been reported with a Group VI element, possibly because of the ill-defined nature of the products that form when alkyl hydrazines are reacted with sulfur dichloride. In the case of aryl hydrazines the mixing of hydrazobenzene with sulfur dichloride and triethylamine leads only to the isolation of azobenzene (5). We now report that the use of functionally substituted hydrazines has permitted the synthesis of two 1,4,2,3,5,6-dithiatetrazines in a facile manner.

Triethylamine in ether was added dropwise to a solution of *sym*-dicarbethoxyhydrazine (Ia) and sulfur dichloride (II) in ether. The resulting triethylamine salt was removed and the solvent evaporated to give tetraethyl 1,4,-2,3,4,6-dithiatetrazine-2,3,5,6-tetracarboxylate (IIIa), m.p. 150° (36%); mol wt: osmotic 425, M^+ 412.0726; ir; 2988 (C-H), 1748 (C=O), 1474, 1440, 1389, 1366 (CH_3), 1260 (C-O), and 760 (N-S) cm^{-1}; nmr: 8.67 (t,12) and 5.69 (q,8)τ. In a similar fashion, di-*t*-butylhydrazine-1,2-diformate (Ib) was converted into the corresponding tetrazine (IIIb), m.p. 170° (40%); ir: 2978 (C-H), 1735 (C=O), 1393 1370, 1362 (t-Bu), 1149 (C-O), 762 and 750 (N-S) cm^{-1}; nmr: 8.47 (s)τ. With *sym*-dicarbobenzyloxyhydrazine (Ic), no reaction occurred at room temperature. Treatment of IIIa with dilute sodium hydroxide returned Ia, which served to confirm the heterocyclic structure. Addition of *m*-chloroperbenzoic acid in chloroform to IIIa formed two new products, tetraethyl 1,1′-sulfonyldi-1,2-hydrazinedicarboxylate (IVa), m.p. 135° (19%); ir: 3328 (N-H), 2984 (C-H), 1755, 1745, 1719 (C=O), 1376 (CH_3), 1321, 1235 (CO), 1200 (SO_2), 775 and 758 (N-S); nmr: 8.77(t,6), 6.00(q,4), 5.94(q,r), and 3.28(s,2)τ, and tetraethyl 1,4,2,3,5,6-dithiatetrazine-2,3,5,6-tetracarboxylate 1,4-dioxide (Va), m.p. 180° (37%); mol wt, M^+ 444.069; ir: 2986 (C-H), 1768 (C=O), 1390, 1368 (CH_3), 1254 (C-O), 1190 (SO?), 743 and 725 (N-S); nmr: 8.70(t,12) and 5.75(q,8) τ. The presence of a sulfoxide moiety in Va was confirmed by means of a positive iodine color test (6,7). The formation of the acyclic compound IVa can be rationalized by assuming the extrusion of sulfur dioxide or sulfur from a cyclic intermediate. Stirring IIIb with anhydrous trifluoroacetic acid afforded sulfur and hydrazine trifluoroacetate (VI).

The conversion of the above substituted tetrazines into the unknown parent system is being studied, and additional details will be described at a later date (8). Finally, an X-ray crystallographic study on IIIb is currently underway here.



Ia-c II IIIa-b IVa + Va

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(7) The reaction involves the conversion of I^- to I_2, thereby producing a dark yellow-brown color. However, IIIa also yields a positive result, as well as depositing S. This result suggests any reducing function can afford a similar false conclusion, and that the test is not completely valid.

(8) All new compounds reported here had satisfactory elemental analyses. Infrared spectra were determined in potassium bromide, while nuclear magnetic resonance measurements used deuteriochloroform as the solvent. Ultraviolet spectra were taken in ethanol; however, only end absorptions were seen. We thank Dr. Jon C. Clardy, Department of Chemistry, Iowa State University, for the double-focusing mass spectra.