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METALLOID DERIVATIVES FOR ORGANIC SYNTHESIS
THE PREPARATION OF URAZOLE AND THIOURAZOLE DERIVATIVES

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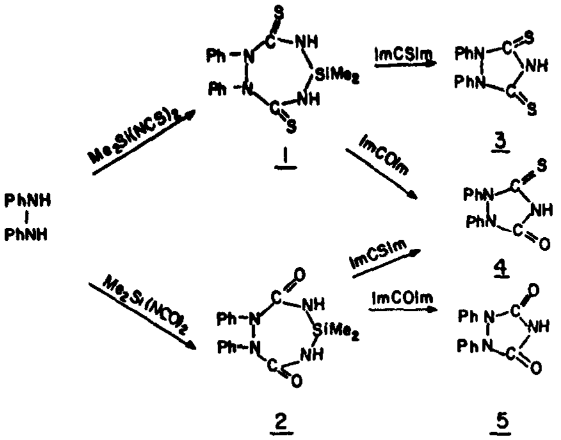
Summary: Silicon isocyanates are introduced as versatile reagents for the mild and efficient conversion of hydrazines to urazole derivatives.

We have recently developed a new method[1] for the conversion of acyclic diamines to triazepine derivatives. The method is based on the use of silicon isocyanates[2] as reagents and covalent templates. As an expansion of this work we wish to report in this communication on the conversion of hydrazines to urazoles. Such ring systems have earlier[3] been prepared by base catalyzed intramolecular condensation of biureas. Application of the new method allows the direct preparation of symmetric and non-symmetric urazoles from exclusively symmetric precursors in a simple, one pot procedure under mild conditions.

The procedure involves the reaction of the hydrazine with silicon isocyanate or thioisocyanate to give the silylated biurea 1 or thiobiurea 2, respectively. These are condensed *in situ* with either carbonyl diimidazole or thiocarbonyl-diimidazole to afford the silylated urazole 5, monothiourazole 4 or dithiourazole 3. Subsequent hydrolysis removes the silyl group and releases the free urazoles.

The experimental procedure is illustrated below for the preparation of 1,2-diphenylurazole[4] 5 from hydrazobenzene.

A solution of hydrazobenzene in benzene (30 ml, 0.12M) was gradually mixed at room temperature with a solution of dimethyl silicon diisocyanate in benzene (20 ml, 0.18M) by the use of a Sage syringe pump (Orion Research Incorporated). The resulting precipitate was then dissolved in 15 ml DMF, treated with a solution of carbonyl diimidazole (10 ml, 0.7M) in DMF and heated under reflux for 30 minutes. Subsequent addition of 16 ml 5% aqueous isopropanol, reflux for another 30 minutes, filtration, (through celite), and concentraiton of the filtrate in vacuo, afforded the crude product 5. This was purified by chromatography on silica gel to give crystalline 5, mp 224°C.



Application of analoguous reaction procedures afforded the hitherto unknown monothiourazole 4 (mp 242 °C) and dithiourazole 3.

Formation of monothiourazole 4 by this method may be visualized by a non-symmetric carbonylation of the intermediate silylated thiobiurea (or biurea) derivative. The carbonyl diimidazole attacks first the nitrogen adjacent to the silyl group, and then the hydrazine nitrogen in a transamidation step, affording the thermodynamically favored five-membered ring compound.

The advantage of this procedure is its adaptability for the preparation of a large variety of ring systems by varying the structure of the hydrazine, silicon pseudohalide and acylating agent, respectively. The scope and limitations of this method for the preparation of other heterocyclic ring systems are under current investigation.

References

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