Group IV Imidazoline Expansion–Contraction Reactions[1]

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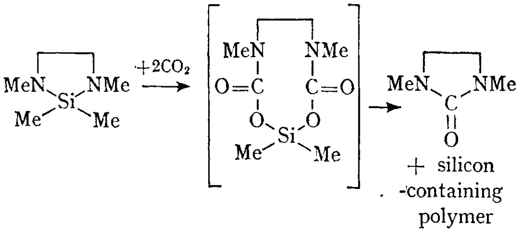
WE are prompted by the recent publication of Cragg and Lappert[2] concerning aminosilylation of unsaturated substrates to make preliminary report of our studies of the action of carbon dioxide on *NN'*-dialkyl-silicon[3] and -germanium[4] imidazolidines. Evidence from n.m.r. spectra recorded during the course of these exothermic reactions indicates that the reaction proceeds in such a way as to preserve the magnetic equivalence of the methylene bridge protons, thus ruling out the presence of significant amounts of stable insertion product containing only one molecule of added carbon dioxide. Distillation of the viscous material from the reaction of 1,2,2,3-tetramethylsilaimidazolidine with carbon dioxide (either added in solid form or bubbled through) gave a liquid (b.p. 101°/14 mm.) which was identified as 1,3-dimethylimidazolid-2-one.[5] A glassy silicon-containing residue was left behind. We formulate the reaction sequence as:



The analogous boron-containing nine-membered-ring compound is known.[6] We have observed similar exothermic reactions between silicon and germanium imidazolidines and phenyl isocyanate, both neat and in ether.

Expansion–contraction processes involving the action of carbon disulphide on organic *NN'*-dialkylimidazolidines proceed *via* unsymmetrical seven-membered-ring insertion products which are thermally unstable with respect to conversion into cyclic thioureas.[7]

Portions of the experimental work were performed by G. T. Cocks.

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[1] Portions of this investigation have been reported at the 148th American Chemical Society Meeting, Chicago, August, 1964, and at the Second International Symposium on Organometallic Chemistry, Madison, Wisconsin, September, 1965.

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[5] W. R. Boon, *J. Chem. Soc.*, 1947, 307.

[6] R. H. Cragg, M. F. Lappert, and B. P. Tilley, *J. Chem. Soc.*, 1964, 2108.

[7] R. A. Donia, J. A. Shotton, L. O. Bentz, and G. E. P. Smith, *J. Org. Chem.*, 1948, **14**, 946, 952.