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# THERMAL ISOMERIZATION OF CYCLOPROPYL-SUBSTITUTED SILANES

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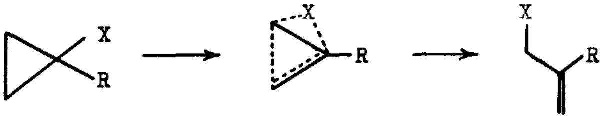
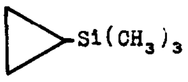
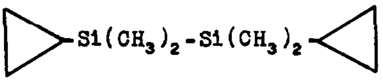
In a recent communication (1), Grant and Swinbourne have reported that cyclopropyl chloride and bromide isomerized mainly to allyl chloride and bromide in gas phase respectively. This observation with the kinetic evidence led to a suggestion that isomerization occurred by ring opening associated with halogen atom migration. Related studies of thermal isomerization of 1,1-dibromo-2,3-dimethylcyclopropane (2) and 1,1-dichlorocyclopropanes (3,4) gave supports to the suggestion. Evidences in these cases are the separation of halogen atoms during the reaction (3,4) and the first order kinetics (4).



We are now reporting the first examples of thermal isomerization of cyclopropyl-substituted silanes to allylsilanes, which represent an interesting contrast to the behavior of alkylcyclopropanes in thermolysis.



(I)



(II)

Cyclopropyltrimethylsilane (I) prepared from cyclopropyllithium and trimethylchlorosilane was passed slowly through a quartz tube heated at 450°. The reaction mixture was collected in a trap immersed in a liquid-nitrogen bath. Allyltrimethylsilane was formed in 95 % yield based on the consumed I.

The isomerization of 1,2-dicyclopropyltetramethyldisilane (II), prepared from cyclopropyllithium and 1,2-dichlorotetramethyldisilane, b.p. 92.0°(25 mm Hg), $n_D^{20}$ 1.4760, $d_4^{20}$ 0.8465, under similar conditions gave the same sort of results. Examination of the reaction mixture from II by v.p.c. revealed that II isomerized to 1-cyclopropyl-2-allyltetramethyldisilane (III), b.p. 83° (19 mmHg), $n_D^{20}$ 1.4723, $d_4^{20}$ 0.8284, and subsequently to 1,2-diallyltetramethyldisilane (IV), b.p. 86°(24 mmHg), $n_D^{20}$ 1.4712, $d_4^{20}$ 0.8132. Neither propenyl nor isopropenyl derivatives formed. In a typical run, 35.3 mmoles of II was converted to 9.20 mmoles of III and 1.45 mmoles of IV along with 14.6 mmoles of unchanged II at 450°.

As an interesting contrast to these observations, thermal isomerization of cyclopropane itself and its alkyl derivatives gave products formed by ring opening followed by unselective migration of hydrogen (5). For example, methyl-, ethyl-, and fluorocyclopropane isomerized to mixtures of the corresponding allyl-, cis- and trans-propenyl-, and isopropenyl derivatives (1).

Related works are in progress. All new compounds gave satisfactory elemental analyses and will be described in details later.

## References

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