

PRELIMINARY COMMUNICATION

THE REACTION OF TRIMETHYLSILYL AND TRIMETHYLGGERMYL RADICALS WITH OLEFINS

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Reactions involving attack of R_3M^\cdot radicals, with $M = Si, Ge, \text{ or } Sn$, on an olefin, as in Eqn (1), are of considerable importance in synthesis, and interest attaches to the possibility of the reversal of the initial attachment. Approximate ΔH values for the addi-



tion of Me_3M^\cdot radicals to ethylene, have been estimated¹ for $M = Si, Ge, \text{ and } Sn$ respectively to be $-18, +3 \text{ and } +5 \text{ kcal} \cdot \text{mole}^{-1}$. Addition of R_3Sn^\cdot radicals to olefins is known to be reversible at room temperature², and we have now found that, in accord with the ΔH values, with Me_3Si^\cdot radicals the reaction is essentially irreversible, even at 140° , but with Me_3Ge^\cdot radicals, while there is no detectable reversal at 40° , there is substantial reversal at temperatures of 80° and higher.

Photolysis of bis(trimethylgermyl)mercury in excess of 1-hexene at 40° gave 15% of hexamethyldigermene, about 14% of 1-hexyltrimethylgermane, a little 1-hexenyltrimethylgermane, several higher boiling organic products, and 100% of mercury. When *cis*-1-deuterio-1-hexene was used, the recovered olefin showed no isomerization. The corresponding reactions at 80 and 100° gave slightly smaller amounts of 1-hexyltrimethylgermane and larger amounts of hexamethyldigermene, and the infrared spectrum of the recovered deuterated olefin showed that about one-third had been isomerized from *cis* to *trans*. The internal olefin 4-methyl-2-pentene gave similar results, no isomerization occurring at 40° , partial isomerization at 60° and 80° , and complete isomerization at $100, 125, \text{ and } 140^\circ$ to an equilibrium mixture containing 16% of the *cis*-isomer. The same mixture was reached starting either from the *cis*- or from the *trans*-olefin.

In the corresponding reactions with bis(trimethylsilyl)mercury, addition of the Me_3Si^\cdot radicals to double bonds again occurred, but there was no isomerization of either olefin in the temperature range $40\text{--}140^\circ$.

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REFERENCES

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