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Chemistry of Germanium Atoms. V. Deoxygenation of Carbonyl Compounds by Germanium Vapor (Atom)

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Synopsis. The co-condensation of thermally evaporated germanium vapor with carbonyl compounds was found to yield olefins and germanium monoxide.

Studies of metal-vapor reactions have been of considerable interest in organometallic chemistry and organic synthesis during the last few decades.[1] With this type method, it is proving to be feasible to synthesize organometallic compounds which would be difficult, if not impossible, to prepare by other methods and to study their reactive intermediates.

The study of a carbon atom as the homologue of a germanium atom has been well investigated, while the chemical properties of a germanium atom have been little studied.[2-7] In studying the reaction of germanium atoms in the condensed phase, we have found that germanium vapor (atom) abstracts oxygen atom from carbonyl compounds.

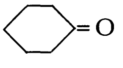
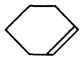
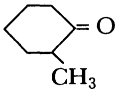
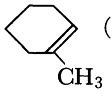
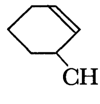
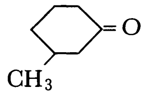
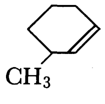
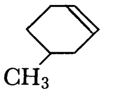
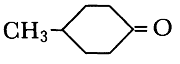
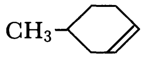
In this paper, we first describe the deoxygenation of carbonyl compounds by germanium vapor (atom).

Results and Discussion

The reaction of thermally vaporized germanium atoms with carbonyl compounds was examined. The results are summarized in Table 1.

The reaction of germanium atoms with acetone produced propylene (1.0%) and germanium monoxide.[8] Other aliphatic ketones showed a similar behavior; the reactions of germanium atoms with 3-pentanone, 2-pentanone, and 4-heptanone gave 2-pentene (3.6%), 1-pentene (3.6%) and 2-pentene (5.0%), and 3-heptene (2.6%), respectively, shown in Table 1. With cyclohexanone and methylcyclohexanones, germanium atoms gave cyclohexene and methylcyclohexenes (0.4—2.0%) as expected, and germanium monoxide. Other products, in addition to olefins and germanium monoxide, were negligible (>0.1%) in the reactions of germanium atoms with carbonyl compounds.

Table 1. The Reaction of Germanium Atoms with Carbonyl Compounds

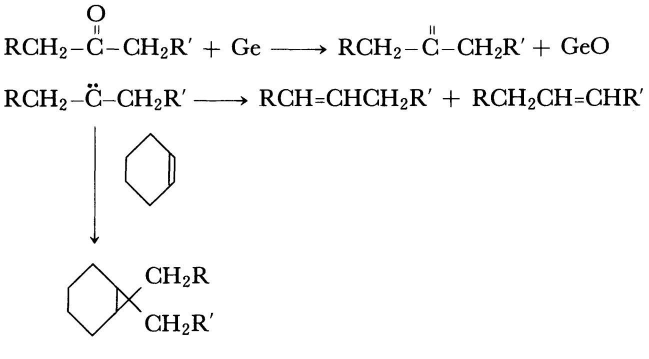
Substrate	Product (Yield/%)[a]
$CH_3\,COCH_3$	$CH_3CH{=}CH_2$ (1.0)
$C_2H_5COC_2H_5$	$C_2H_5CH{=}CHCH_3$ (3.6)
$CH_3COC_3H_7$	$CH_2{=}CHC_3H_7$(3.6), $CH_3CH{=}CHC_2H_5$ (5.0)
$C_3H_7COC_3H_7$	$C_2H_5CH{=}CHC_3H_7$ (2.6)
	 (0.5)
	 (0.4),  (1.2)
	 (0.8),  (0.4)
	 (2.0)

a) GLC yields. Yields of products were determined on the basis of the amount of the germanium metal consumed on the assumption that all of the germanium metal completely reacted with carbonyl compounds.

Blank experiments were carried out under identical conditions. As a result, the products shown in Table 1 were attributable to the interaction of germanium atoms with the starting carbonyl compounds.

The products, olefins shown in Table 1 are strong evidence for the intermediacy of carbenes in the deoxygenation of carbonyl compounds by germanium vapor (atoms). The carbenes are known to rearrange to isomeric olefins.[9,10]

When a mixture of carbonyl compounds and a large excess of cyclohexene as a carbene trapping reagent was used as a matrix for germanium vapor (atoms), no peak of 7,7-dialkylnorcaranes was detected by GC-MS. The yields of the olefins produced were almost constant, despite the presence of cyclohexene. These results indicate that a ketone may complete for germanium atoms in the presence of an olefin and that intramolecular stabilization of alkylcarbenes by product formation is more rapid than an olefin addition, even at −196 °C.



$$RCH_2-\overset{\overset{O}{\|}}{C}-CH_2R' + Ge \longrightarrow RCH_2-\ddot{C}-CH_2R' + GeO$$

$$RCH_2-\ddot{C}-CH_2R' \longrightarrow RCH{=}CHCH_2R' + RCH_2CH{=}CHR'$$

Scheme 1.

The deoxygenation of oxygen-containing compounds by germanium vapor (atoms) can be rationalized in terms of the large value of the heat of combination of a germanium atom with an oxygen atom (155 kcal mol^{-1}, 1 cal=4.184 J).[11]

Similar results have been reported for the co-condensation of carbon atoms with carbonyl compounds.[12-14]

It is interesting that our results indicate no distinction between thermally generated germanium atoms and nucleogenetic carbon atoms based on the reaction with carbonyl compounds.

Experimental

The reaction apparatus and conditions employed in this study have been described previously (ca. 1200—1300 °C, 5×10^{-3} Torr, 1 Torr=133.322 Pa).[5] In a typical experiment 0.5 g (6.9 mmol) of germanium metal was evaporated at a rate of ca. 10 mg·min^{-1} while an excess of acetone (ca. 15 cm^3) was co-condensed on the walls of a reaction flask containing an alumina-coated tungsten crucible and a perforated inlet tube through which acetone was introduced as vapor. The reaction flask was immersed in liquid nitrogen during the germanium evaporation. After germanium evaporation and the introduction of acetone were completed, the flask was warmed to room temperature and allowed to stand for 1.5 h.

The reaction mixture was fractionated by low-pressure trap-to-trap distillation on a vacuum line. The products were identified by comparing their GC-MS and retention times on GLC with those of authentic samples. The amounts of products were calculated by GLC with an internal-standard method.

GLC analyses were performed on a Shimadzu GC-4A and 8A gas chromatograph equipped with a 2-m column packed with 20% SE-30 or 20% squalane. GC-MS were obtained with a JEOL JMS-DX 303 mass spectrometer and data analyses were performed on a JMN-DA 5000 mass data system.

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