CHEMISTRY LETTERS, pp. 1685-1686, 1986.

Insertion Reactions of Dimethylgermanone [$(CH_3)_2Ge{=}O$] into Si-O and Si-Cl Bonds

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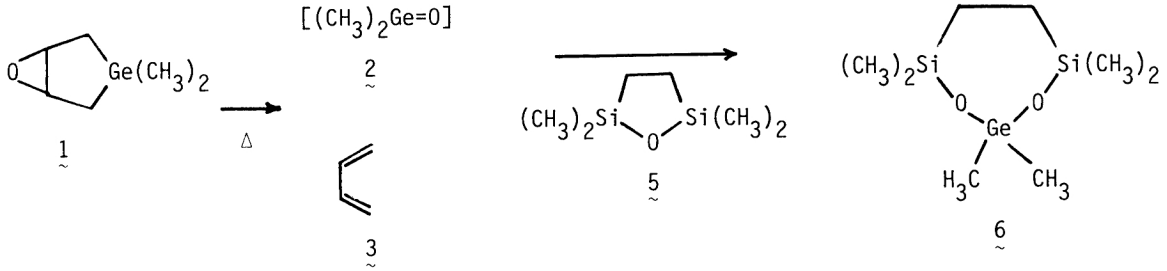
Flash vacuum co-pyrolysis (FVP) of 3,3-dimethyl-6-oxa-3-germabicyclo[3,1,0]hexane with various trapping reagents has been carried out. Adducts which result from insertion of dimethylgermanone into Si-O and Si-Cl bonds have been outlined.

The reaction chemistry of germanones, reactive intermediates which possess a germanium oxygen double bond is limited.[1)]

Pyrolysis of 3,3-dimethyl-6-oxa-3-germabicyclo[3,1,0]hexane (1) has been shown to yield butadiene (3) and hexamethylcyclotrigermoxane (4).[2)] The formation of 4 has been suggested to result from the cyclotrimerization of dimethylgermanone (2). We report two new insertions reaction of 2 into Si-O and Si-Cl bonds. These reactions have been carried out by FVP of 1 with various trapping reagents in the gas phase at 580° and 10^{-4} mm pressure. For example, FVP of 1 and 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane (5) gave 2,2,4,4,7,7-hexamethyl-1,3-dioxa-2-germa-4,7-disilacycloheptane (6) (40%) and 3. Properties of 6: ^{1}H NMR ($CDCl_3$) δ = 0.068 (s, 12H), 0.524 (s, 6H), 0.695 (s, 4H); ^{13}C NMR δ = 0.535 (4C, CH_3Si), 3.30 (2C, CH_3Ge), 11.98 (2C, CH_2Si); IR (NaCl) ν = 1005 and 980 cm^{-1} Si-O-Ge; mass spectrum (rel. intensities) m/e 267 (6.6%), 265 (23.7%), 263 (17.1%), 261 (12.2%) P-15$^+$, 240 (3.9%), 239 (26.7%), 237 (100%), 235 (73.8%), 233 (52.2%), 149 (6.3%), 148 (5.8%), 147 (34.2%), 133 (23.4%), 131 (15.4%), 119 (20.1%), 117 (16.4%), 115 (14.4%), 103 (11.8%); high resolution mass spectrum: calcd. for $C_7H_{19}O_2{}^{74}Ge^{28}Si_2$ 265.0135; found 265.0135. The formation of 6 probably results from the insertion of 2 into one of the Si-O bonds of 5. While 5 is a strained heterocyclic siloxane this is not an essential for insertion of 2 into siloxane (Si-O-Si) bonds. The FVP of 1 and



1,3-diphenyltetramethyldisiloxane gave bis(phenyldimethylsiloxy)dimethylgermane (7) (15%) and 2. Properties of 7: ^{1}H NMR δ = 0.308 (s, 12H), 0.417 (s, 6H), 7.3-7.6 (m, 10H); mass spectrum (rel. intensities) 393 (10.5%), 391 (36.9%), 389 (26.1%), 387 (17.9%) P-15$^+$, 245 (10.7%), 244 (7.5%), 243 (52.2%), 242 (16.9%), 241 (39.0%), 239 (29.7%), 183 (21.6%), 181 (100%), 179 (74.6%), 177 (58.9%); high resolution mass spectrum: calcd. for $C_{17}H_{25}O_2{}^{74}Ge^{28}Si_2$ 391.0605; found 391.0601.

On the other hand, FVP of 1 and phenyldimethylmethoxysilane (8) gave 3, 4 and recovered 6. Apparently, Si-O bonds of siloxanes are more reactive than Si-O bonds of alkoxysilanes towards insertion of 2. By comparison, dimethylsilanone [$(CH_3)_2Si$=O] inserts into both siloxane and alkoxysilane Si-O bonds.[3,4]

2 also inserts into Si-Cl bonds. For example, FVP of 1 and t-butyldimethylchlorosilane gave t-butyldimethylsiloxydimethylchlorogermane (9) (23%) and 2. Properties of 9: ^{1}H NMR δ = 0.057 (s, 6H), 0.837 (s, 6H), 0.858 (s, 9H); ^{13}C NMR δ = -2.29 (2C, CH_3Si), 7.43 (2C, CH_3Ge), 18.81 (1C, C), 26.125 (3C, $(CH_3)_3$); IR ν = 975 cm^{-1} Si-O-Ge; mass spectrum (rel. intensities) m/e 217 (6.5%), 216 (4.8%), 215 (43.4%), 214 (17.7%), 213 (100%), 212 (25.5%), 211 (77.9%), 209 (48.5%) P-57$^+$. High resolution mass spectrum: calcd for $C_4H_{12}O^{35}Cl^{74}Ge^{28}Si$ 212.9558; found 212.9555.

$$t\text{-}Bu(CH_3)_2Si\text{-}Cl + [(CH_3)_2Ge{=}O] \longrightarrow t\text{-}Bu(CH_3)_2Si\text{-}O\text{-}Ge(CH_3)_2Cl$$

A description of the FVP experiment can be found in Ref. 5.

This work was supported by the U.S. Air Force Office of Scientific Research 86-0042. K.T.K. thanks the Korean Science and Engineering Foundation. G.M. and W.P.W. thank NATO 845/83.

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(Received July 5, 1986)