ylene reduction does take place quite efficiently when a molybdenum porphyrin is used.[15,16]

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Cleavage of Silicon–Silicon and Germanium–Germanium Bonds with 1,2-Dibromoethane by a Free-Radical Mechanism. Evidence for Bimolecular Homolytic Substitution at Silicon and Germanium[1]

Sir:

Recent stereochemical, kinetic, and esr studies have shown that bimolecular homolytic substitution ($S_{H}2$) reactions may take place at a multivalent metallic center of the group II–V elements.[2] However, no example of this process for organosilicon and organogermanium compounds has been reported to date in spite of the fact that such compounds are very common. This is probably due to their possessing stronger element–carbon bonds than those of other organometallic compounds. For example, while benzylstannanes undergo extensive Sn–C bond cleavage,[2h] $S_{H}2$ reactions will take place only at benzylic hydrogen[3] when the corresponding benzylsilanes are treated with *N*-bromosuccinimide. We thought that the silicon–silicon bond, like oxygen–oxygen[4] and sulfur–sulfur[5] bonds, could be susceptible to the $S_{H}2$ reaction since the bond energy of Si–Si is considerably lower than that of Si–C.[6]

$$X\cdot + MR_n \longrightarrow XMR_{n-1} + R\cdot \qquad (1)$$

After several unsuccessful attempts,[7,8] we have now obtained clear-cut evidence for the $S_{H}2$ reaction at silicon and germanium in solution. The reaction stems from chain reactions involving attack of a bromine atom generated from 1,2-dibromoethane on an organodisilane to give a bromosilane and a silyl radical.

In a typical experiment, a mixture of 3.64 mmol of hexamethyldisilane (**1a**) and 6.35 mmol of 1,2-dibromoethane was irradiated for 0.5 hr by a 450-W high-pressure mercury arc lamp at room temperature in the presence of a catalytic amount (0.1 mmol) of dibenzoyl peroxide (BPO). The course of the reaction was characterized by the evolution of almost the theoretical amount (70.3 ml at normal temperature and pressure, 96.6%) of ethylene. Examination of the mixture by vpc and nmr revealed that 6.51 mmol (100%) of trimethylbromosilane was the sole product, along with small amounts of unchanged **1a** (0.39 mmol) and 1,2-dibromoethane (3.10 mmol). A similar result was obtained by a thermally induced reaction. Thus, 16.01 mmol (100%) of trimethylbromosilane and 7.99 mmol (99.8%) of ethylene together with 2.02 mmol of unchanged **1a** and 2.10 mmol of 1,2-dibromoethane were obtained from a mixture of **1a** (10.01 mmol) and 1,2-dibromoethane (10.11 mmol) by heating at 90° for 45 min in the presence of 0.088 mmol of BPO.

$$Me_3SiSiMe_3 + BrCH_2CH_2Br \xrightarrow[\text{heat, or } h\nu]{\text{BPO}} 2Me_3SiBr + CH_2{=}CH_2 \qquad (2)$$

A number of organodisilanes were then examined. All disilanes examined gave the corresponding bromosilanes quantitatively.

$$\underset{\mathbf{1}}{R_1R_2R_3SiSiR_4R_5R_6} + BrCH_2CH_2Br \xrightarrow[\text{heat, or } h\nu]{\text{BPO}} R_1R_2R_3SiBr + R_4R_5R_6SiBr + CH_2{=}CH_2 \qquad (3)$$

1a, $R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = CH_3$
b, $R_1 = H$; $R_2 = R_3 = R_4 = R_5 = R_6 = CH_3$
c, $R_1 = R_4 = H$; $R_2 = R_3 = R_5 = R_6 = CH_3$
d, $R_1 = Ph$; $R_2 = R_3 = R_4 = R_5 = R_6 = CH_3$
e, $R_1 = R_2 = Ph$; $R_3 = R_4 = R_5 = R_6 = CH_3$
f, $R_1 = R_4 = Ph$; $R_2 = R_3 = R_5 = R_6 = CH_3$
g, $R_1 = R_2 = R_3 = Ph$; $R_4 = R_5 = R_6 = CH_3$
h, $R_1 = R_2 = R_4 = R_5 = Ph$; $R_3 = R_6 = CH_3$
i, $R_1 = PhCH_2$; $R_2 = R_3 = R_4 = R_5 = R_6 = CH_3$
j, $R_1 = c\text{-}C_3H_5$; $R_2 = R_3 = R_4 = R_5 = R_6 = CH_3$
k, $R_1 = R_4 = c\text{-}C_3H_5$; $R_2 = R_3 = R_5 = R_6 = CH_3$

Hexamethyldigermane also reacts with 1,2-dibromoethane in the presence of BPO at 90°, or at room temperature under irradiation, to give a quantitative yield of trimethylbromogermane and ethylene.

$$Me_3GeGeMe_3 + BrCH_2CH_2Br \longrightarrow 2Me_3GeBr + CH_2{=}CH_2 \qquad (4)$$

Many bonds of group IVb elements to the transition metals are cleaved by halogens, halogen acids, and a variety of organic halides including 1,2-dibromoethane.[9] Complexes having germanium bonded to Cu, Ag, Au, Pd, or Pt all react quantitatively with 1,2-dibromoethane,[10] the mechanism being believed to proceed through a multicenter transition state.[11] Group IVb mercurials of the type $(R_3M)_2Hg$ (R = Me, M = Si;[12] R = Ph, M = Si;[13] R = Me, M = Ge;[14] and R = Ph, M = Ge[15]), antimony derivatives, $(Ph_3Si)_3Sb$[16a] and

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$(Et_3Si)_3Sb$,[16b] and bismuth derivatives, $(Ph_3Si)_3Bi$,[16a] have also been shown to react with 1,2-dibromoethane to give ethylene, along with the corresponding metal and R_3MBr (M = Si or Ge). A concerted mechanism has also been suggested recently for the reaction of mercurials.[12]

We propose, however, a free-radical chain mechanism for the reaction of organodisilanes with 1,2-dibromoethane that involves the attack of a bromine atom on the Si–Si bond.[17] Bromine atoms are generated from β-bromoethyl radicals, which are in turn derived from 1,2-dibromoethane by bromine abstraction with the silyl radicals.

$$Br\cdot + R_3SiSiR_3 \longrightarrow BrSiR_3 + R_3Si\cdot \qquad (5)$$

$$R_3Si\cdot + BrCH_2CH_2Br \longrightarrow R_3SiBr + \cdot CH_2CH_2Br \qquad (6)$$

$$\cdot CH_2CH_2Br \longrightarrow CH_2{=}CH_2 + Br\cdot \qquad (7)$$

The following facts support the mechanism. Although hexamethyldisilane, one of the most reactive organodisilanes, did not undergo reaction with 1,2-dibromoethane, even after prolonged heating without initiators in the dark at 90°, a small amount of BPO catalyzed the reaction markedly, an apparent kinetic chain length being estimated as 80–100. Irradiation with a 450-W high-pressure mercury arc lamp also initiated the reaction slowly. Since even in the presence of BPO, galvinoxyl[18] inhibits the reaction completely, this is strongly indicative of the free-radical nature of the reaction. The reaction can be carried out in benzene and in cyclohexane, but in carbon tetrachloride no such bond cleavage occurs. This is rationalized by considering a competing chlorine abstraction from carbon tetrachloride by silyl radicals,[19] the resulting trichloromethyl radical being capable only of dimerizing under the present reaction conditions.

$$R_3Si\cdot + CCl_4 \longrightarrow R_3SiCl + CCl_3\cdot \qquad (8)$$

$$2CCl_3\cdot \longrightarrow Cl_3CCCl_3 \qquad (9)$$

An alternative mechanism may be considered that involves a low concentration of bromine produced by the decomposition of 1,2-dibromoethane. Subsequently, bromine may react with disilanes to cleave the silicon–silicon bond. The slow production of

$$Br\cdot + BrCH_2CH_2Br \longrightarrow Br_2 + \cdot CH_2CH_2Br \qquad (10)$$

$$Br_2 + Me_3SiSiMe_3 \longrightarrow 2Me_3SiBr \qquad (11)$$

bromine in a similar system has been suggested in the bromine-sensitized photochemical decomposition of 1,2-dibromotetrachloroethane.[20] However, a bromine

$$Br\cdot + BrCCl_2CCl_2Br \longrightarrow Br_2 + \cdot CCl_2CCl_2Br \qquad (12)$$

atom could not abstract bromine from 1,2-dibromoethane because it would be endothermic by 35 kcal[21] and thus reaction 10 cannot be an effective propagation step in the long chain. Furthermore, bromine ought to cleave not only the silicon–silicon bond but also the phenyl–silicon bond(s) when phenyl-substituted disilanes (**1d–h**) are subjected to the reaction; however, no such cleavage of phenyl groups was observed with these compounds. In fact, treatment of **1h** with bromine resulted in phenyl–silicon rather than silicon–silicon cleavage,[22] while the present reaction yielded diphenylmethylbromosilane almost quantitatively.

Hexamethyldigermane behaves quite similarly to **1a** and hence we believe that free trimethylgermyl radicals[23] are also key intermediates.

$$Br\cdot + Me_3GeGeMe_3 \longrightarrow Me_3GeBr + Me_3Ge\cdot \qquad (13)$$

$$Me_3Ge\cdot + BrCH_2CH_2Br \longrightarrow Me_3GeBr + \cdot CH_2CH_2Br \qquad (14)$$

Finally we note that these reactions are also useful in synthetic organosilicon chemistry. Thus, bromosilanes such as dimethylbromosilane and methyldiphenylbromosilane, which are difficult or at least tedious to prepare by other methods, can be obtained easily in high yield.[24]

The structure of disilanes and their reactivity will be discussed in a forthcoming paper.

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Unusual Metalloporphyrins IX. Preparation of a New (Mesoporphyrin IX dimethyl esterato)dinitrosylruthenium(II)

Sir:

There has been considerable biological interest in the interaction of nitric oxide with ferro- or ferriheme,[1,2] ferro- or ferrihemochromes,[1,3] as well as iron–porphyrin bound to proteins.[1,3,4] Magnetic measurements on a nitric oxide derivative of hemoglobin[5] have shown that this complex has only one unpaired electron, whereas NO–ferricytochrome c was shown to be diamagnetic.[6] Recently esr solution spectroscopy has shown that nitric oxide derivatives of ferrihemochrome,[3] hemoglobin,[3,7] myoglobin,[3] and ferrocytochrome c[3,8] have one unpaired electron.

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