

ORGANOGERMANIUM COMPOUNDS

II*. REDUCTION OF ORGANIC HALIDES WITH HYDROGERMANES

HIDEKI SAKURAI, KUNIO MOCHIDA, AKIRA HOSOMI AND FUMIO MITA**

Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980 (Japan)

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SUMMARY

The scope of the reduction of organic halides with trialkylgermanes under homolytic condition has been studied. Germanium hydrides can reduce polyhaloalkane without catalysts under mild conditions, the homolytic mechanism being, however, established for the uncatalyzed reduction. The observed orders of reactivity and selectivity in the reduction are consistent with a radical chain mechanism involving free germyl radicals. Some synthetic applications are described.

INTRODUCTION

Reduction of organic halides involving halogen abstraction reaction by silicon and tin radicals has been investigated extensively, and the synthetic utility of these reductions, especially with organotin hydrides, has been widely established². Alkyl halides can be reduced to alkanes by organogermanium hydrides in radical chain reactions³, but, no detailed investigation of these reactions has been carried out previously, probably because germanium hydrides are less readily available than other Group IVb hydrides. In extension of our investigations on silyl radicals⁴, we have examined the stereochemistry⁵, relative reactivities⁶, and synthetic applications of germyl radicals. In this paper we describe the scope of the reduction of organic halides by organogermanium hydrides.

RESULTS AND DISCUSSION

Hydrogermanes are capable of reducing organic halides simply by heating without free-radical initiators, in contrast to the behavior of hydromonosilanes⁷. The uncatalyzed reduction of alkyl halides by alkylgermanes was first reported by Lesbre and Satgé^{8,9} and a free-radical chain process was suggested recently as a possible mechanism¹⁰. The following experiments demonstrated more clearly the free-radical mechanism for reduction. Thus, addition of a small amount of a free-radical scavenger

* For part I, see ref. 5.

** Department of Synthetic Chemistry, Kyoto University.

such as galvinoxyl¹¹ resulted in complete inhibition of the reduction of carbon tetrachloride, one of the most reactive organic halides, with triethylgermane at 80°. This is a strong indication of a free-radical nature of the uncatalyzed reaction. Furthermore, while triethylsilane alone did not react with an excess of carbon tetrachloride on heating at 80°, addition of triethylgermane resulted in almost quantitative conversion of both germane and silane to the corresponding chlorides, and again the reaction was inhibited by galvinoxyl. These results may be interpreted in terms of the following chain process.

TABLE 1

REDUCTION OF CHLOROALKANES WITH TRIMETHYL CHLORIDE INITIATED BY BPO OR DTBP^a

| Run | Reactants | Mmoles | Products | Mmoles | Recovered | Mmoles |
|-----|---|--------|---|--------|--|--------|
| 1 | CCl ₄ | 0.61 | CHCl ₃ | 0.58 | CCl ₄ | Trace |
| | Me ₃ GeH | 0.71 | Me ₃ GeCl | 0.61 | | |
| | BPO ^b | None | CH ₂ Cl ₂ | Trace | | |
| 2 | CCl ₄ | 1.15 | CHCl ₃ | 0.88 | CCl ₄ | 0.30 |
| | Me ₃ GeH | 0.89 | Me ₃ GeCl | 0.90 | | |
| | BPO | 0.01 | | | | |
| 3 | CH ₂ ClCHClCH ₃ | 2.34 | CH ₂ ClCH ₂ CH ₃ | 0.33 | CH ₂ ClCHClCH ₃ | 0.89 |
| | Me ₃ GeH | 0.82 | CH ₃ CHClCH ₃ | 0.17 | | |
| | BPO | 0.07 | Me ₃ GeCl | 0.53 | | |
| 4 | CH ₂ ClCHClCH ₃ | 0.60 | CH ₂ ClCH ₂ CH ₃ | 0.21 | CH ₂ ClCHClCH ₃ | 0.11 |
| | Me ₃ GeH | 0.58 | CH ₃ CHClCH ₃ | 0.13 | | |
| | DTBP ^c | 0.07 | Me ₃ GeCl | 0.53 | | |
| 5 | cyclo-C ₆ H ₁₁ Cl | 1.74 | cyclo-C ₆ H ₁₂ | 0.03 | cyclo-C ₆ H ₁₁ Cl ^d | |
| | Me ₃ GeH | 0.59 | Me ₃ GeCl | 0.07 | | |
| | BPO | 0.09 | | | | |
| 6 | cyclo-C ₆ H ₁₁ Cl | 0.68 | cyclo-C ₆ H ₁₂ | 0.45 | cyclo-C ₆ H ₁₁ Cl | 0.16 |
| | Me ₃ GeH | 0.51 | Me ₃ GeCl | 0.51 | | |
| | DTBP | 0.05 | | | | |
| 7 | Cl(CH ₂) ₄ Cl | 0.34 | C ₄ H ₉ Cl | 0.06 | Cl(CH ₂) ₄ Cl ^d | |
| | Me ₃ GeH | 0.79 | Me ₃ GeCl | 0.14 | | |
| | DTBP | 0.12 | | | | |
| 8 | Cl(CH ₂) ₂ Cl | 0.88 | C ₄ H ₉ Cl | 0.51 | Cl(CH ₂) ₂ Cl | 0.48 |
| | Me ₃ GeH | 0.58 | Me ₃ GeCl | 0.74 | | |
| | DTBP | 0.13 | | | | |
| 9 | CHCl ₂ CH ₂ Cl | 1.32 | CH ₂ ClCH ₂ Cl | 0.54 | CHCl ₂ CH ₂ Cl | 0.55 |
| | Me ₃ GeH | 0.72 | Me ₃ GeCl | 0.64 | | |
| | BPO | 0.13 | | | | |
| 10 | CHCl ₂ CH ₂ Cl | 0.97 | CH ₂ ClCH ₂ Cl | 0.34 | CHCl ₂ CH ₂ Cl | 0.49 |
| | Me ₃ GeH | 0.46 | Me ₃ GeCl | 0.47 | | |
| | DTBP | 0.19 | | | | |
| 11 | PhCH ₂ Cl | 0.18 | PhCH ₃ | 0.20 | PhCH ₂ Cl ^d | |
| | Me ₃ GeH | 1.13 | Me ₃ GeCl | 0.24 | | |
| | BPO | 0.02 | | | | |
| 12 | PhCH ₂ Cl | 0.76 | PhCH ₃ | 0.62 | PhCH ₂ Cl ^d | |
| | Me ₃ GeH | 0.62 | Me ₃ GeCl | 0.61 | | |
| | DTBP | 0.13 | | | | |

^a Reaction time was 20 h. ^b At 80°. ^c At 135°. ^d Not determined.



The nature of the initiation step is uncertain, but probably a trace amount of oxygen plays a role.

Reduction of organic halides with organogermanium hydrides proceeds satisfactorily in the presence of free-radical initiators such as dibenzoyl peroxide (BPO) and di-tert-butyl peroxide (DTBP). The reaction can be, therefore, best explained in terms of a free-radical chain process, involving an initiation step followed by propagation steps such as reactions (2) and (3). Table 1 summarizes the product distribution in the reduction of chloroalkanes as determined by VPC, and Table 2 shows the reduction of alkyl bromides and iodides, and clearly indicates the selectivity of the process.

Polychloroalkanes are reduced stepwise, which makes it possible to carry out the selective reduction of polychloride. The reactivity of the halogen atoms falls

TABLE 2

REDUCTION OF BROMOALKANES AND IODOALKANES WITH TRIMETHYLGERMANE INITIATED BY DTBP (135°, 20 h)

| Run | Reactants | Mmoles | Products | Mmoles | Recovered | Mmoles | | |
|-----|---|--------|--------------------------------------|--------|---|--------|---|------|
| 1 | Cl(CH ₂) ₃ Br | 0.63 | C ₃ H ₇ Cl | Trace | Cl(CH ₂) ₃ Br | 0.53 | | |
| | Me ₃ GeH | 0.48 | | | | | | |
| | DTBP | None | Me ₃ GeBr | Trace | | | | |
| 2 | Cl(CH ₂) ₃ Br | 1.09 | C ₃ H ₇ Cl | 0.61 | Cl(CH ₂) ₃ Br | 0.42 | | |
| | Me ₃ GeH | 0.64 | Me ₃ GeBr | 0.55 | | | | |
| | DTBP | 0.05 | | | | | | |
| 3 | Cl(CH ₂) ₄ Br | 0.87 | C ₄ H ₉ Cl | 0.34 | Cl(CH ₂) ₄ Br | 0.14 | | |
| | Me ₃ GeH | 0.98 | Me ₃ GeBr | 0.58 | | | | |
| | DTBP | 0.01 | | | | | | |
| 4 | Cl(CH ₂) ₄ Br | 0.42 | C ₄ H ₉ Cl | 0.34 | Cl(CH ₂) ₄ Br | 0.14 | | |
| | Me ₃ GeH | 0.40 | Me ₃ GeBr | 0.18 | | | | |
| | DTBP | 0.10 | | | | | | |
| 5 | cyclo-C ₆ H ₁₁ I | 1.44 | cyclo-C ₆ H ₁₂ | 0.90 | cyclo-C ₆ H ₁₁ I | 0.51 | | |
| | Me ₃ GeH | 1.01 | Me ₃ GeI | 0.76 | | | | |
| | DTBP | 0.08 | | | | | | |
| 6 | cyclo-C ₆ H ₁₁ I | 1.26 | cyclo-C ₆ H ₁₂ | 0.89 | cyclo-C ₆ H ₁₁ I | 0.37 | | |
| | cyclo-C ₆ H ₁₁ Br | 0.75 | Me ₃ GeBr ^a | | | | cyclo-C ₆ H ₁₁ Br | 0.53 |
| | Me ₃ GeH | 1.18 | Me ₃ GeI ^a | | | | | |
| | DTBP | 0.15 | | | | | | |
| 7 | cyclo-C ₆ H ₁₁ Br | 1.04 | cyclo-C ₆ H ₁₂ | 0.71 | cyclo-C ₆ H ₁₁ Br | 0.19 | | |
| | cyclo-C ₆ H ₁₁ Cl | 1.19 | Me ₃ GeBr | 0.68 | | | cyclo-C ₆ H ₁₁ Cl | 1.01 |
| | Me ₃ GeH | 0.95 | | | | | | |
| | DTBP | 0.26 | | | | | | |

^a Not determined.

in the order: I > Br > Cl. These features are in accord with that found in homolytic reduction of organic halides with organotin hydrides¹². Nagai, Shiojima, Nishiyama and Matsumoto reported that alkyl iodides were not reduced by silicon hydrides¹³. Germanium hydrides reduced even monochloroalkanes smoothly. Thus, the reactivity of the germanium hydrides in these reductions more resembles that of the tin hydrides.

The (secondary)C-Cl/(primary)C-Cl selectivity in the reduction of 1,2-dichloropropane by trimethylgermane was 1.6-1.9; a similar range was observed in reduction of 1,2,3-trichloropropane with silicon hydrides (1.5)¹².

Germanium hydrides may be synthetically useful in reduction of organic halides because of their moderate reactivity combined with high selectivity. Hydrogen-halogen exchange reactions catalyzed by peroxides are also useful in the preparation of germanium halides. For example, 1-naphthylphenylmethylbromogermane¹⁴ was prepared in a quantitative yield from the corresponding hydrogermane by heating to reflux in dibromomethane or in bromoform in the presence of a catalytic amount of DTBP. The bromogermane was obtained as a pure solid by evaporation of the

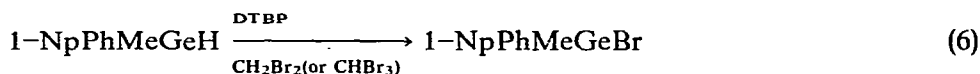


TABLE 3

REDUCTION OF HALOBENZENES WITH TRIMETHYLGERMANE INITIATED BY DTBP (135°, 20 h)

| Run | Reactants | Mmoles | Products | Mmoles |
|-----|----------------------------------|--------|---|--------|
| 1 | C ₆ H ₅ F | 2.02 | C ₆ H ₆ | 0 |
| | Me ₃ GeH | 1.08 | C ₆ H ₅ GeMe ₃ | 0 |
| | DTBP | 0.47 | Me ₃ GeGeMe ₃ | 0.14 |
| 2 | C ₆ H ₅ F | 2.04 | C ₆ H ₆ | 0 |
| | Me ₃ GeH | 1.11 | C ₆ H ₅ GeMe ₃ | 0 |
| | DTBP | 0.31 | Me ₃ GeGeMe ₃ | 0.11 |
| 3 | C ₆ H ₅ Cl | 1.74 | C ₆ H ₆ | 0.09 |
| | Me ₃ GeH | 1.12 | C ₆ H ₅ GeMe ₃ | 0.11 |
| | DTBP | 0.10 | Me ₃ GeCl | 0.17 |
| 4 | C ₆ H ₅ Cl | 0.64 | C ₆ H ₆ | 0.09 |
| | Me ₃ GeH | 0.55 | C ₆ H ₅ GeMe ₃ | 0.16 |
| | DTBP | 0.29 | Me ₃ GeCl | 0.23 |
| 5 | C ₆ H ₅ Br | 1.81 | C ₆ H ₆ | 0.67 |
| | Me ₃ GeH | 1.20 | Me ₃ GeBr | 0.96 |
| | DTBP | 0.74 | | |
| 6 | C ₆ H ₅ Br | 0.66 | C ₆ H ₆ | 0.35 |
| | Me ₃ GeH | 0.44 | Me ₃ GeBr | 0.34 |
| | DTBP | 0.06 | | |
| 7 | C ₆ H ₅ I | 1.07 | C ₆ H ₆ | 0.34 |
| | Me ₃ GeH | 0.49 | Me ₃ GeI | 0.25 |
| | DTBP | 0.06 | | |
| 8 | C ₆ H ₅ I | 1.08 | C ₆ H ₆ | 0.88 |
| | Me ₃ GeH | 1.04 | Me ₃ GeI | 0.61 |
| | DTBP | 0.43 | | |

volatile materials. Without catalysts, the reaction did not go to completion, which made the separation of bromide from hydride rather cumbersome.

Table 3 shows the results of reduction of aromatic halides with trimethylgermane catalyzed by DTBP. Fluorobenzene was not reduced under the conditions used. Iodobenzene, bromobenzene and chlorobenzene were reduced to benzene, the ease of reaction decreasing in the sequence $\text{PhI} > \text{PhBr} > \text{PhCl} \gg \text{PhF}$.

Chlorobenzene gave a condensation product, phenyltrimethylgermane, in addition to benzene. The question of whether or not the reduction involves direct abstraction of halogen from the benzene ring is of interest, and we plan to discuss the mechanism in detail in a future publication.

EXPERIMENTAL

Trialkylchlorogermanes and trialkylgermanes

Trimethylchlorogermane and triethylchlorogermane were prepared from the respective tetraalkylgermanes as described previously¹⁵. These were reduced with lithium aluminum hydride to give trimethylgermane, b.p. 28°, and triethylgermane, 123–124°.

Uncatalyzed reduction of carbon tetrachloride with a mixture of triethylgermane and triethylsilane

Et_3SiH (0.322 g, 2.77 mmoles) and Et_3GeH (0.075 g, 0.466 mmole) were dissolved in an excess of CCl_4 , and the solution was divided into three equal parts, [A], [B] and [C]. [A] was kept in a refrigerator, while [B] and [C] were heated at 80° for 1 h with or without a small amount of galvinoxyl, respectively. Careful examination by VPC revealed that [A] and [B] did not contain Et_3SiCl nor Et_3GeCl , whereas almost quantitative conversion of both hydrides to the corresponding chlorides was observed for [C]. A similar experiment on Et_3GeH also confirmed the inhibition of the reaction by adding galvinoxyl.

Preparation of 1-naphthylphenylmethylbromogermane

A mixture of 1-naphthylphenylmethylgermane (14.0 g, 48 mmoles) and DTBP (0.5 g, 3.5 mmoles) was dissolved in methylene bromide (20 g, 126 mmoles), the solution being heated at 135–140° for 15 h. After evaporation of volatile materials at 70°/30 mm, 17.5 g (48 mmoles, 100%) of 1-naphthylphenylmethylbromogermane was obtained as a pure solid, m.p. 59–62° (lit.¹⁴. 58–60°).

Reaction procedure and analysis of products

Reactions were carried out usually in small glass ampoules, and products were analyzed by VPC. For example, a mixture of cyclohexyl chloride (0.080 g, 0.68 mmole), trimethylgermane (0.061 g, 0.51 mmole), and DTBP (0.008 g, 0.05 mmole) was sealed in an ampoule which was placed in an oil bath thermostatted at $135 \pm 1^\circ$. After 20 h the ampoule was opened and n-octane (0.020 g, 0.178 mmole) was added as internal standard. Yields of cyclohexane (0.45 mmole, 66%), trimethylchlorogermane (0.51 mmole, 100%), and recovered cyclohexyl chloride (0.16 mmole, 24%) were determined by VPC by measurement of peak areas in conjunction with the internal standard and calibration with authentic samples.

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