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A novel phenyl–bromine ligand exchange reaction on germanium by boron tribromide

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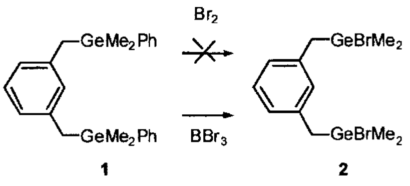
A novel phenyl–bromine ligand exchange reaction by BBr_3 on germanium was investigated that proceeds without breaking Ge–CH_2Ar bond. Typically, the reaction between $(PhCH_2)_3PhGe$ and BBr_3 resulted exclusively in the formation of $(PhCH_2)_3GeBr$. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: organogermanium compound; synthesis; phenyl–bromine exchange; boron tribromide

INTRODUCTION

As part of an extensive study of novel heteroditopic hosts in which a germanium moiety acts as an anion-capturing site,[1–6] we wanted to prepare, as an intermediate for germanium-containing calixarene, 1,3-bis[(bromodimethylgermyl)methyl]benzene (**2**) by the reaction between 1,3-bis[dimethyl(phenyl)germylmethyl] benzene (**1**) and bromine (Eq. 1). Though it is known that tetraphenylgermane (**3**) can be conveniently converted to bromotriphenylgermane (**4**)[7] and/or dibromodiphenylgermane (**5**)[8] depending on the reaction condition, the reaction between **1** and bromine failed to give **2**. Spectroscopic analysis of the reaction mixture indicated that the Ge–CH_2Ar bond was cleaved. The use of other brominating reagents, such as *N*-bromosuccinimide (NBS), also caused cleavage of the Ge–CH_2Ar bond.



(1)

It occurred to us that use of BBr_3 instead of bromine might solve this problem, since Haubold *et al.*[9] reported that the reaction between an aryltrimethylsilane and boron trihalide gave aryldihaloborane and trimethylsilyl halide:

(2)

Though the purpose of the reaction in Eq was to prepare an arylborane, this reaction can be regarded as a phenyl–halogen ligand exchange on silicon. Thus, this reaction should be able to be applied to a phenyl–bromine ligand exchange reaction on germanium:

(3)

Haubold *et al.*[9] also reported that BBr_3 was a mild reagent that showed high selectivity. Thus, we could expect that this reagent would be useful for our purpose. Our preliminary attempt to introduce bromine in **1** was successful when we used BBr_3 instead of bromine. The reaction with BBr_3 afforded the desired **2** in 48% yield without cleaving the Ge–CH_2Ph bond. In this paper we describe the scope and limitation of this exchange reaction.

RESULTS AND DISCUSSION

We chose benzyltriphenylgermane (**6**), dibenzyldiphenylgermane (**7**) and tribenzylphenylgermane (**8**) as the samples to examine whether the phenyl–bromine exchange reaction will proceed without cleaving the Ge–CH_2Ph bond by use of BBr_3. The same ligand exchange reaction was attempted with **3** for comparison.

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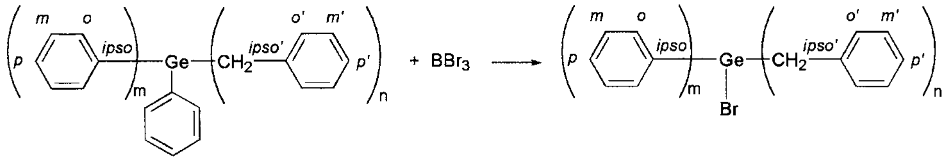

6: m = 2; n = 1
7: m = 1; n = 2
8: m = 0; n = 3

9: m = 2; n = 1
10: m = 1; n = 2
11: m = 0; n = 3

Scheme 1.

The reaction of **3** with BBr_3 (equimolar amount) in CH_2Cl_2 proceeded smoothly to afford exclusively **4** in a 93% yield. It is noteworthy that no polybromogermanes were obtained, indicating that the reaction ceased when one phenyl group was exchanged with bromine, even if phenyl group(s) remained unexchanged.

The reaction between **6, 7** or **8** and BBr_3 was carried out in a similar manner, except that the amount of BBr_3 used was 1 : 1 to 1 : 4 (BBr_3 in excess). In all cases, a substantial amount of resinous by-products was formed. However, it was always possible to isolate the desired monobromogermanes in pure form by extensive use of gel-permeation chromatography (GPC). Thus, benzylbromodiphenylgermane (**9**), bromodibenzylphenylgermane (**10**) and tribenzylbromogermane (**11**) were obtained from **6, 7** and **8** respectively (Scheme 1). The yields of the bromogermanes are listed in Table 1.

The yield of bromogermanes depends on the amount of BBr_3 used to some extent, but use of equimolar BBr_3 will be recommended in view of cost/performance. In all cases, no isolable amount of polybromogermanes was formed. The low yield may in part be due to the hydrolysis of the bromide formed during the workup. (One of the referees kindly suggested that the low yield can be explained by the fact that bromogermanes are usually susceptible to hydrolysis by water. It would be better to use 30–40% HBr to increase the yield.)

In the case of the reaction between **6** and BBr_3, it was found that the yield of **9** was much the same when the reaction was carried out at 0 °C or at ambient temperature with stirring, whereas the reaction at 50 °C with stirring gave a substantially lower yield. Much the same was true for the other reactions. The reaction was continued for 1, 2, 3, and 4 h. The longer the reaction time, the better the yield up to 4 h. If the reaction was continued for more than 4 h, however, the yields tend to be lower.

Table 1. The yield of the ligand-exchanged products

Germane	BBr_3 used[a]	Bromogermane	Yield (%)
3	1	**4**	93
6	1	**9**	22
6	3	**9**	28
6	4	**9**	23
7	1	**10**	35
7	2	**10**	30
7	3	**10**	17
7	4	**10**	15
8	1	**11**	25
8	3	**11**	31

[a] Amount of BBr_3 used relative to 1 mol of germanes.

Compounds **8–11** were characterized mostly based on ^1H and ^{13}C NMR spectroscopy.

This ligand exchange reaction with BBr_3 will have a wide application in organogermanium chemistry, whether $Ge–CH_2Ar$ bonds are present or not. Tetrachlorogermane, $GeCl_4$, is an important starting material in organogermanium chemistry that is commercially available at an affordable cost. The reaction between $GeCl_4$ and phenylmagnesium bromide affords **3**, which is often the starting material for a variety of organogermanium compounds. A method by which one can introduce bromine on germanium without affecting other substituents will have a very wide application, since a bromine atom bonded to germanium may be relatively easily converted to other substituents.

CONCLUSION

It was established that BBr_3 can bring about phenyl–bromine ligand exchange on germanium without breaking the coexisting $Ge–CH_2Ph$ bonds. Furthermore, this ligand exchange reaction will terminate when one phenyl group is exchanged even if two or more phenyl groups are bonded to germanium. To the best of our knowledge, there has been no prior report of a phenyl–bromine ligand exchange reaction using BBr_3 and, hence, no report of one without cleavage of the $Ge–CH_2Ar$ bond. A study to expand the scope of this reaction is in progress in our laboratory.

EXPERIMENTAL

General methods

^1H NMR spectra were measured on a JEOL ECX-500 spectrometer operating at 500 MHz, and the chemical shifts were reported in δ (ppm) with respect to Me_4Si. ^{13}C NMR spectra were determined at 125 MHz on the same spectrometer. Mass spectra were recorded on a JEOL

NS-MP09 mass spectrometer operating in the electron impact (EI) mode at 70 eV. Elemental analysis was carried out by the Microanalytical Laboratory, Department of Chemistry, The Graduate School of Science, the University of Tokyo.

Bis[dimethyl(phenyl)germylmethyl]benzene (1)

A CCl_4 (350 ml) solution of *m*-xylene (31.8 g; 0.3 mol), NBS (112.2 g; 0.63 mol) and a catalytic amount of azobisisobutyronitrile was refluxed. When a vigorous reaction ceased, refluxing was continued for 30 min. After cooling, the solid was filtered off and the filtrate was concentrated, to which ethanol was added to give colorless crystals of bis(*m*-bromomethyl)benzene (30.0 g; 38.0%).

To a mixture of magnesium (0.85 g; 35.0 mmol), bromodimethylphenylgermane (10.4 g; 40.0 mol), and hexamethylphosphoramide (2 ml) in tetrahydrofuran (THF; 8 ml), there was added, under nitrogen, a quarter of a THF (40 ml) solution of bis(*m*-bromomethyl)benzene (3.96 g; 15.0 mmol). 1,2-Dibromoethane (0.2 ml) was added to initiate the reaction. The rest of the bis(*m*-bromomethyl)benzene solution was added dropwise, and the mixture was refluxed for another 2 h. The mixture was cooled and hydrolyzed with 30% acetic acid. The product was extracted with diethylether (100 ml) which was washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4. The solvent was removed and the residue was distilled *in vacuo* (200–220 °C/7 Torr) to afford colorless oil of **1** (5.36 g; 77.1%). ^{1}H NMR ($CDCl_3$): δ 7.41–6.61, (m, 14H, ArH), 2.34 (s, 4H, $-CH_2Ge$), 0.30 (s, 12H, Ge–CH_3). ^{13}C NMR ($CDCl_3$): δ 141.1, 140.3, 133.2, 128.4, 128.0, 127.9, 127.4, 123.8 (Ar), 25.4 ($-CH_2Ge$), −4.0 ($GeCH_3$). EI mass spectrometry (MS) *m*/*e* 466 ($M^+ = 466$). It must be added that MS shows a complex pattern due to the isotope distribution characteristic for compounds containing two germanium atoms.[10]

1,3-Bis[(bromodimethylgermyl)methyl]benzene (2)

To a CH_2CH_2 (20 ml) solution of **1** (1.5 g; 3.2 mmol), BBr_3 (1 mol dm^{-3} CH_2CH_2 solution: 6.4 ml; 6.4 mmol) was added dropwise under a nitrogen stream with the aid of a gas-tight syringe. The mixture was stirred for 2 h at room temperature. Water (50 ml) was added to the mixture and the product was extracted with CH_2CH_2 (50 ml × 2). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed. The residue was distilled *in vacuo* (250 °C/7 Torr) and purified with preparative high-performance liquid chromatography (column GPC, elute $CHCl_3$) to give **2** (0.73 g; 48.7%) as a pale yellow liquid.

^{1}H NMR ($CDCl_3$): δ 7.16–6.86 (m, 4H, ArH), 2.73 (s, 2H, $-CH_2Ge$), 0.76 (s, 6H, Ge–CH_3). ^{13}C NMR ($CDCl_3$): δ 137.4, 128.5, 127.4, 124.8, 30.4 ($-CH_2Ge$), 3.1 ($GeCH_3$). EIMS *m*/*e* 468 ($M^+ = 468$).

Compound **6** was prepared by the method that was described as benzyl Grignard method in the literature:[11] m.p. 79.5–80 °C (lit.[10,11] m.p. 85–86.5 °C).

Dibenzyldiphenylgermane (7)

Compound **7** was obtained from **5** in a similar manner to that of **6** in 70% yield; m.p.: 35 °C. Though the synthesis of **7** was previously reported,[12] the melting point was not given. ^{1}H NMR ($CDCl_3$): δ 2.69 (s, 4H), 6.85–7.28 (m, 20H). ^{13}C NMR ($CDCl_3$): δ 22.4, 124.4, 127.9, 128.1, 128.6, 128.8, 134.7, 136.8, 139.1.

Tribenzylphenylgermane (8)

Trichloro(phenyl)germane was prepared by a literature method[13] in 41% yield, b.p. 90 °C/1.2 kPa; lit. 103 °C/1.6 kPa. Benzyl chloride (55.8 g, 0.44 mol) in Et_2O at room temperature was added dropwise to a solution of magnesium turnings (7.9 g, 0.33 mol) in Et_2O (80 ml) under an atmosphere of nitrogen. The mixture was stirred for 2 h, after which trichloro(phenyl)germane (8.0 g, 0.03 mmol) in Et_2O (40 ml) was added dropwise. The solution was refluxed for 3 h and the solvent evaporated. The residue was heated under reduced pressure (250 °C/1.2 kPa) to remove any volatile material. From the residue, yellow crystals of **8** (10.9 g, 0.026 mol, 87%) were obtained; m.p.: 60 °C. EIMS *m*/*z* 424 (M^+ $C_{27}H_{26}{}^{74}Ge$, 424.12). Anal. Found: C, 76.95; H, 6.30. Calc. for $C_{27}H_{26}Ge$: C, 76.65; H, 6.19°. ^{1}H NMR ($CDCl_3$): δ 2.42 (s, 6H), 6.85–7.27 (m, 20H). ^{13}C NMR ($CDCl_3$): δ 22.0, 124.3, 127.8, 128.2, 128.4, 128.6, 134.0, 138.1, 139.4.

Reaction between tetraphenylgermane (3) and BBr_3

To a solution of **3** (1.90 g, 5.0 mmol) in $CHCl_3$ (100 ml) under an atmosphere of nitrogen, BBr_3 (5.0 ml of a 1.0 mol dm^{-3} solution in CH_2Cl_2, 5.0 mmol) below 0 °C was added dropwise. The mixture was stirred for 3 h at room temperature and water was then added. The organic layer was extracted with CH_2Cl_2, dried and evaporated. The residue was distilled under reduced pressure (210 °C/0.9 kPa) to yield white needles of bromotriphenylgermane (**4**), in 93% yield; m.p. 137 °C (lit.[7] 138.5 °C). ^{1}H NMR ($CDCl_3$): δ 7.41–7.46, 7.62–7.64. ^{13}C NMR ($CDCl_3$): δ 128.6 (*meta*; d), 130.4 (*para*; d), 134.1 (*ortho*; d), 134.6 (*ipso*; s).

Reaction between benzyltriphenylgermane (6) and BBr_3

To a solution of **6** (1.98 g, 5.0 mmol) in CH_2Cl_2 (35 ml) was reacted with BBr_3 (5.0 ml, 1 mol dm^{-3} in CH_2Cl_2 solution, 5.0 mmol) in a similar manner as described above to yield a pale yellow oil of benzylbromodiphenylgermane (**9**; 0.44 g, 1.11 mmol, 22%). EIMS, *m*/*z*: 398 ([M+]). $C_{19}H_{17}{}^{79}Br^{74}Ge$, 397.97. ^{1}H NMR ($CDCl_3$): δ 3.19 (CH_2; s, 2H), 7.02–7.48 (arom; m, 15H). ^{13}C NMR ($CDCl_3$): δ 28.9 (CH_2; t), 125.4 (*para′*; d), 128.2 (*meta′*; d), 128.4 (*ortho′*; d), 128.8 (*meta*; d), 130.2 (*para*; d), 133.8 (*ortho*; d), 134.7 (*ipso*; s), 136.1 (*ipso′*; s).

Reaction between dibenzyldiphenylgermane (7) and BBr_3

To a solution of **7** (2.05 g, 5.0 mmol) in CH_2Cl_2 (35 ml) was reacted with BBr_3 (5.0 ml, 1 mol dm^{-3} in CH_2Cl_2 solution, 5.0 mmol) in a similar manner as above to yield a colorless oil of dibenzylbromophenylgermane (**10**; 0.71 g, 1.72 mmol, 35%). EIMS, *m/z*: 412 ([M^+]: $C_{20}H_{19}{}^{79}Br^{74}Ge$, 411.9). ^1H NMR ($CDCl_3$): δ 2.91 (CH_2; s, 4H), 7.00–7.37 (arom; m, 15H). ^{13}C NMR ($CDCl_3$): δ 27.9 (CH_2; t), 125.4 (*para′*; d), 128.2 (*meta′*; d), 128.4 (*ortho′*; d), 128.7 (*meta*; d), 130.0 (*para*; d), 133.4 (*ortho*; d), 135.2 (*ipso*; s), 136.3 (*ipso′*; s).

Reaction between tribenzylphenylgermane (8) and BBr_3

BBr_3 (5.0 ml of a 1.0 mol dm^{-3} solution in CH_2Cl_2, 5.0 mmol) was added to **8** (2.12 g, 5.0 mmol) in CH_2Cl_2 (35 ml) at 0 °C, and the mixture was stirred at various temperatures in an atmosphere of nitrogen. Water was added to consume the BBr_3, and the organic layer was separated off. The aqueous layer was further extracted with CH_2Cl_2, the organic layers were combined, dried over anhydrous Na_2SO_4, and evaporated. The crude product was treated with preparative GPC to give a pale yellow oil of tribenzylbromogermane (**11**; 0.53 g, 1.24 mmol, 31%). EIMS *m/z*: 426 (M^+). $C_{21}H_{21}{}^{79}Br^{74}Ge$, 426.0. ^1H NMR ($CDCl_3$): δ 2.65 (s, 6H), 6.98–7.26 (m, 15H). ^{13}C NMR ($CDCl_3$): δ 27.1, 125.4 (*para*; d), 128.6 (*meta*; d), 128.6 (*para*; d), 136.6 (*ipso*; s). Though compound **11** was previously described in the literature,[14] neither spectroscopic data nor the synthetic procedure were reported.

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