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# Preparation and Some Reactions of Diarylgermylenedialkali Metals

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The reactions of diarylgermanes with alkali metals in HMPA/THF or THF were found to give the corresponding diarylgermylenedialkali metals in high yields. Diphenylgermylenedipotassium reacted with aryl halides or carbonyl compounds to give reduction products predominantly. With alkyl halides, diphenylgermylenedipotassium gave mainly substitution products.

The reactions of organogermylalkali metals with organic halides or carbonyl compounds are useful for the formation of carbon–germanium bonds.[1–10] Because of its importance, the study of organogermylalkali metals has been reviewed.[1] Among them, however, there are only a few reports regarding organogermylenedialkali metals (probably due to the lack of a useful preparative method). For example, Krause and Carney examined the reaction of germane ($GeH_4$) with sodium in liquid ammonia but only suggested the probable existence of germylenedisodium ($GeH_2Na_2$).[11] Cross and Glockling found the reaction of tetrabenzylgermane with lithium in ethylene glycol dimethyl ether or butyllithium to yield dibenzylgermylenedilithium in 7.8% or 2% yields, respectively.[12] Recently, Bulten and Noltes have reported briefly on the reaction of dibutyldichlorogermane with potassium in HMPA to give dibutylgermylenedipotassium in 22% yield.[13] Yields of organogermylenedialkali metals reported are low and the reactions of organogermylenedialkali metals with organic substrates remain to be disclosed.

In this paper, we present the preparation of diarylgermylenedialkali metals from diarylgermanes and alkali metals in HMPA/THF or THF in high yields and then the reactions of diphenylgermylenedipotassium with organic halides and carbonyl compounds.

## Results and Discussion

*Preparation of Diarylgermylenedialkali Metals.* Diarylgermylenedialkali metals ($Ar_2GeM_2$, **1**, Ar= $C_6H_5$, *p*-$CH_3C_6H_4$, M=Li, Na, K) were prepared from the corresponding diarylgermanes ($Ar_2GeH_2$) and alkali metals in HMPA/THF or THF. The color of **1** was reddish brown ($\lambda_{max}$ 320 nm in case of diphenylgermylenedipotassium).

**I**, thus prepared, was characterized by the following experiments: (1) $^1H$ and $^{13}C$ NMR of **1**, and (2) the formation of diarylgermanes-$d_2$ by hydrolysis of **1** with $D_2O$.

$$Ar_2GeH_2 + 4M \xrightarrow[\text{or THF}]{\text{HMPA/THF}} Ar_2GeM_2 + 2MH \qquad (1)$$

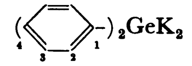
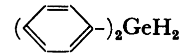
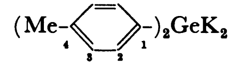
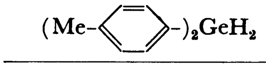
$$Ar = C_6H_5,\ p\text{-}CH_3C_6H_4,\ M = Li,\ Na,\ K$$

$$Ar_2GeM_2 \xrightarrow{D_2O} Ar_2GeD_2 \qquad (2)$$

(1) $^1H$ and $^{13}C$ NMR parameters of diphenylgermylenedipotassium ($Ph_2GeK_2$, **1a**) and di (*p*-tolyl)germylenedipotassium (($p$-$CH_3C_6H_4)_2GeK_2$, **1b**) are summarized in Table 1, together with those of the starting materials. The chemical shifts of aromatic protons in **1a** and **1b** in comparison with those of the corresponding diarylgermanes are shifted slightly to a higher field, while those of C-1 carbon drastically to a lower field. The observed shifts may be due to the unusual charge distribution; $Ar_2Ge^{\delta-}K_2^{\delta+}$ in comparison with $Ar_2Ge^{\delta+}H_2^{\delta-}$. Thus, negative charge on the aromatic ring may produce an upfield shift of aromatic protons and downfield shift of C-1 carbon. Such phenomena for NMR spectra of organometallic compounds have been reported.[14–18]

(2) It is well known that organogermanium hydrides are formed quantitatively by hydrolysis of

Table 1. $^1H$ and $^{13}C$ NMR data of diarylgermylenedipotassium and diarylgermanes in THF-$d_8$

| Compound | $^1H$ NMR | | | $^{13}C$ NMR | | | | |
|---|---|---|---|---|---|---|---|---|
| | Ge-Ph | Ge-H | Me | C-1 | C-2 | C-3 | C-4 | Me |
|  | 6.48—7.79<br>(*m*) | | | 164.0 | 138.3 | 127.6 | 124.3 | |
|  | 7.15—7.64<br>(m, 5H) | 4.99<br>(s, 1H) | | 135.7 | 137.7 | 130.2 | 130.9 | |
|  | 6.51—7.48<br>(dd, 4H) | | 2.11<br>(s, 3H) | 160.0 | 138.7 | 128.8 | 133.0 | 22.7 |
|  | 6.99—7.50<br>(dd, 4H) | 4.91<br>(s, 1H) | 2.25<br>(s, 3H) | 140.7 | 137.0 | 131.0 | 132.4 | 22.6 |

organogermylalkali metals.[1] Therefore, the formation and yield of organogermanium hydrides after hydrolysis can be regarded as those of organogermylalkali metals. The yields of **1** were estimated to be 83—96% on the basis of those of diarylgermanes-$d_2$ formed by hydrolysis of **1** with $D_2O$.

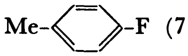
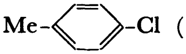
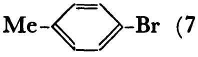
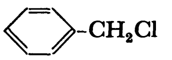
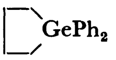
*Reactions of Diphenylgermylenedipotassium,* **1a**. Reactions of **1a** with organic halides and carbonyl compounds were examined at room temperature for 30 min. Hydrolysis of the reaction mixtures led to reduction products, substitution products, digermanes, and polymers containing germanium. Products were isolated by preparative GLC and TLC, and identified by comparing their IR, NMR, and retention times on GLC with those authentic samples.

Reactions of **1a** with halotoluenes (halogen=Br, Cl, and F) were examined. Reactions of **1a** with bromotoluene gave toluene in 127.7% yield. Digermanes and polymers were also formed. However, no substitution products, diphenylditolylgermane or diphenyltolylgermane, were detected. Reaction of **1a** with chlorotoluene gave toluene in 3.6% yield. No tolylgermanes were formed. Diphenylgermane obtained by hydrolysis of **1a** was recovered in 45.9% yield, and digermanes and polymers were observed. With fluorotoluene, **1a** gave neither toluene nor tolylgermanes. Diphenylgermane was found in 47.1% yield. Digermanes and polymers were formed. The yield of toluene in the reactions of **1a** with halotoluenes increased in the order Br>Cl>F.

In contrast, reactions of **1a** with alkyl halides or benzyl chloride gave predominantly substitution products. Reduction products were also formed as minor products. Reactions of **1a** with alkyl bromides or iododes gave predominantly dialkyldiphenylgermanes. Alkyldiphenylgermanes were minor products. Similarly, dibenzyldiphenylgermane was formed in the reaction of **1a** with benzyl chloride mainly. On the other hand, **1a** reacted with alkyl chlorides to give alkyldiphenylgermanes predominantly. However, **1a** reacted with *t*-butyl chloride to give no *t*-butylgermanes. No diphenylgermane was recovered. Digermanes and polymers were formed. Furthermore, **1a** reacted with 1,4-dibromobutane or 1,5-dibromopentane to give 1,1-diphenylgermacyclopentane or 1,1-diphenylgermacyclohexane, respectively. These results are summarized in Table 2. In a separate experiment, reactions of KH which can be produced in the preparation of **1a** from diphenylgermane and potassium with organic halides were also examined under similar conditions. KH reacted with bromotoluene to give toluene in 10—15% yield. With chlorotoluene, benzyl chloride, or alkyl halides, no reduction products were formed.

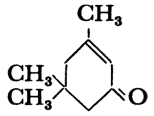
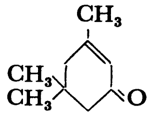
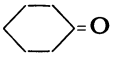
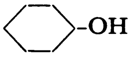
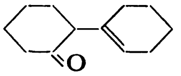
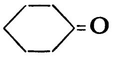
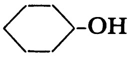
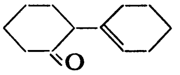
With carbonyl compounds, **1a** gave reduction products and aldol condensation products as the main products. Unidentified substitution products were also formed as minor products. Digermanes and polymers were again observed. In a separate experiment, KH was found to react with carbonyl compounds to give aldol condensation products under similar conditions, but no reduction products. There-

TABLE 2. REACTIONS OF DIPHENYLGERMYLENEDIPOTASSIUM WITH ORGANIC HALIDES[a)]

| Reactant (mmol) | | Products,[c)] Yield/% | | | |
|---|---|---|---|---|---|
| $Ph_2GeK_2$[b)] | RX | R-H | $Ph_2Ge(H)R$ | $Ph_2GeR_2$ | $Ph_2GeH_2$ |
| 0.535 |  (7.35) | 0 | 0 | 0 | 47.1 |
| 0.535 |  (7.41) | 3.6 | 0 | 0 | 45.9 |
| 0.535 |  (7.39) | 127.7 | 0 | 0 | 0 |
| 0.534 | EtCl (excess) | d) | 60.1 | 33.3 | 0 |
| 0.534 | EtBr (7.40) | d) | 24.9 | 65.4 | 0 |
| 0.534 | EtI (2.70) | d) | 32.7 | 51.5 | 0 |
| 0.507 | *i*-PrCl (6.30) | d) | 82.8 | 0 | 0 |
| 0.534 | *n*-BuBr (7.50) | d) | 25.6 | 58.1 | 0 |
| 0.712 | *t*-BuCl (8.20) | d) | 0 | 0 | 0 |
| 0.507 | *n*-$C_8H_{17}$Br (6.30) | 8.4 | 38.0 | 61.4 | 0 |
| 0.813 |  (4.88) | 2.4 | 0 | 60.3 | 0 |
| 0.709 | $Br(CH_2)_4Br$ (7.64) | 0 | 0 |  23.6 | 0 |
| 0.709 | $Br(CH_2)_5Br$ (7.47) | 0 | 0 |  13.5 | 0 |

a) The reactions were carried out at room temperature for 30 min. The yields of products were based on the concentrations of consumed $Ph_2GeK_2$. b) The concentration of $Ph_2GeK_2$ was determined by that of $Ph_2GeD_2$ by hydrolysis with $D_2O$. c) Digermanes and polymers contained germanium were also formed. d) The yields of products could not be determined by GLC.

Table 3. Reactions of diphenylgermylenedipotassium and KH with carbonyl compounds[a)]

| Reactants (mmol) | | Products (Yield/%)[b)] | |
|---|---|---|---|
| $Ph_2GeK_2$ (0.527)[c)], | $(CH_3)_2CO$ (2.11) | $(CH_3)_2CHOH$ (trace), |  (76.0) |
| KH (24.9), | $(CH_3)_2CO$ (86.1) | $(CH_3)_2CHOH$ (0) |  (41.0) |
| $Ph_2GeK_2$ (0.527), | $PhCOCH_3$ (2.11) | $PhCH(OH)CH_3$ (54.0), | $PhCOCH_2PhCHCH_3$ (57.0) |
| KH (49.9), | $PhCOCH_3$ (200.0) | $PhCH(OH)CH_3$ (0) | $PhCOCH_2PhCHCH_3$ (2.1) |
| $Ph_2GeK_2$ (0.527), | $Ph_2CO$ (2.11) | $Ph_2CHOH$ (30.5) | |
| KH (49.9), | $Ph_2CO$ (86.1) | No products | |
| $Ph_2GeK_2$ (0.527), |  (2.11) |  (12.8) |  (32.0) |
| KH (27.4), |  (50.9) |  (0) |  (12.4) |

a) The reactions were carried out at room temperature for 30 min. The yields of products were based on the concentrations of consumed $Ph_2GeK_2$ and KH. b) Digermanes, polymers, and other unidentified products were also formed. c) The concentration of $Ph_2GeK_2$ was determined by that of $Ph_2GeD_2$ by hydrolysis with $D_2O$.

fore, the reduction products should have arisen from the reaction of **1a** with carbonyl compounds. The results in the reactions of **1a** with carbonyl compounds and KH with carbonyl compounds are summarized in Table 3. The yields of reduction products shown in Table 3 increased in the order benzophenone>acetophenone>acetone.

The results of the reactions of **1a** with organic halides and carbonyl compounds shown in Tables 2 and 3 are different from those of organogermylalkali metals.[1)] It has been reported that organogermylalkali metals react with halotoluenes or carbonyl compounds to give tolylgermanes or organogermylcarbinols as main products, respectively.

The mechanism for the reactions of **1a** with organic halides or carbonyl compounds are not clear. However, taking the formation of reduction products shown in Tables 2 and 3 into consideration, electron transfer between **1a** and organic substrates might be important.

## Experimental

*Materials.* $Ph_2GeH_2$,[19)] $Ph_2GeD_2$,[20)] bp 140—143 °C/0.7 mmHg (1 mmHg≈133.322 Pa), $Ph_2GeBr_2$, bp 115—120 °C/0.15 mmHg,[21)] $Ph_2GeEt_2$, bp 100—108 °C/0.3 mmHg,[22)] $Ph_2Ge(H)Et$, bp 110—115 °C/0.8 mmHg,[23)] $Ph_2GeBu_2$, bp 125 °C/0.4 mmHg,[22)] $Ph_2Ge(H)Bu$, bp 107—109 °C/0.08 mmHg,[23)] $Ph_2Ge(C_8H_{17})_2$, bp 195—198 °C/0.3 mmHg,[24)] $(p\text{-}CH_3C_6H_4)_2GeBr_2$, bp 230—233 °C/13 mmHg,[25)] $Ph_3Ge(C_8H_{17})$, mp 72—73 °C,[26)] 1,1-diphenylgermacyclopentane, bp 118—122 °C/0.15 mmHg,[27)] and 1,1-diphenylgermacyclohexane, bp 118 °C/0.16 mmHg[27)] were prepared as described in the cited references. KH is commercially available.

*Preparation of Di(*p*-tolyl)germane.* A mixture of di(*p*-tolyl)dibromogermane (4.1 g, 0.01 mol) and lithium aluminum hydride (1.0 g, 0.025 mol) in ether (100 cm³) was stirred with reflux for 3 h. After hydrolysis, the organic layer was dried over calcium chloride. The solvent was removed and then fractional distillation gave di(*p*-tolyl)germane (1.9 g, 7.5 mmol, 75.0%), bp 115 °C/2.0 mmHg; $n^{20}$ 1.5839; IR (neat, cm⁻¹) 2050 (Ge-H). Found: C, 65.72: H, 6.46%, Calcd. for $C_{14}H_{16}Ge$: C, 65.46: H, 6.28%.

*Preparation of Diphenyloctylbromogermane.* Diphenyloctylbromogermane was prepared by bromination of triphenyloctylgermane (8.3 g, 0.02 mol) with an equivalent of bromine (3.2 g, 0.02 mol) in refluxing 1,2-dibromoethane (50 cm³) for 2 h. The solvent was removed under reduced pressure, leaving about 10 cm³ of residue. Fractional distillation gave crude diphenyloctylbromogermane (5.8 g, 14 mmol, 69.1%), bp 136—150 °C/0.05 mmHg; NMR (δ in $CDCl_3$) 0.52—1.88 (m, 17H), 6.88—7.78 (m, 10H).

*Preparation of Diphenyloctylgermane.* A mixture of diphenyloctylbromogermane (5.8 g, 14 mmol) and lithium aluminum hydride (1.0 g, 25 mmol) in ether (100 cm³) was stirred with reflux for 3h. After hydrolysis, the organic layer was dried over calcium chloride. The solvent was removed and then fractional distillation gave diphenyloctylgermane (1.3 g, 3.8 mmol, 38.1%), bp 150—158 °C/0.7 mmHg; $n^{20}$ 1.5429; IR (neat, cm⁻¹) 2030 (Ge-H); NMR (δ in $CDCl_3$) 0.35—1.95 (m, 17H), 4.90—5.10 (m, 1H), 6.85—7.95 (m, 10H). Found: C, 70.39; H, 8.35%, Calcd. for $C_{20}H_{28}Ge$: C, 70.44: H, 8.26%.

*Preparation of Isopropyldiphenylgermane.* Isopropylmagnesium chloride was prepared from isopropyl chloride (9.0 g, 0.12 mol) and magnesium (4.0 g, 0.12 g atom) in ether (50 cm³) and benzene (20 cm³). To this Grignard reagent, diphenyldibromogermane (3.9 g, 0.01 mol) dissolved in ether (2 cm$^3$) was added. Toluene (50 cm$^3$) was added dropwise to this reaction mixture, and the ether was replaced immediately by toluene through distillation. The reaction mixture was stirred with reflux for 7 h. After hydrolysis, the organic layer was dried over calcium chloride. The solvent was removed and then fractional distillation gave isopropyldiphenylgermane (1.1 g, 4.06 mmol, 40.6%), bp 100—104 °C/0.4 mmHg; $n^{20}$ 1.5718; IR (neat, cm$^{-1}$) 2025 (Ge-H); NMR ($\delta$ in $CDCl_3$) 0.91—1.40 (d, $J$=6.8 Hz, 6H), 0.65—2.10 (m, 1H), 4.80—5.00 (d, $J$=4.0 Hz, 1H), 6.85—7.75 (m, 10H). Found: C, 66.64: H, 6.79%, Calcd. for $C_{15}H_{18}Ge$: C, 66.51: H, 6.70%.

*Preparation of Dibenzyldiphenylgermane.* Benzylmagnesium chloride was prepared from benzyl chloride (12.7 g, 0.10 mol) and magnesium (2.3 g, 0.1 g atom) in ether (100 cm$^3$). To this Grignard reagent, diphenyldibromogermane (3.9 g, 0.01 mol) dissolved in ether (5 cm$^3$) was added. The reaction mixture was stirred with reflux for 5 h. After hydrolysis, the organic layer was dried over calcium chloride. The solvent was removed and then fractional distillation gave dibenzyldiphenylgermane (0.8 g, 2.0 mmol, 19.6%), bp 156 °C/0.08 mmHg; $n^{20}$ 1.6321; NMR ($\delta$ in $CDCl_3$) 2.61 (s, 1H), 6.54—7.33 (m, 5H). Found: C, 76.46: H, 6.02%, Calcd. for $C_{26}H_{24}Ge$: C, 76.34: H, 5.91%.

*Preparation of Diphenylgermylenedipotassium.* Potassium (1.8 g, 0.046 g atom) was cut into small pieces and placed in the reaction vessel containing anhydrous HMPA (7.5 cm$^3$, 0.045 mol) and THF (11.0 cm$^3$) under argon. The vessel (50 cm$^3$ two-necked flask) was fitted with a condenser, drying tube argon inlet, and pressure equalizing dropping funnel. Diphenylgermane (1.20 g, 5.0 mmol) dissolved in THF (1.0 cm$^3$) was placed in the dropping funnel. The reaction vessel was blanketed with argon and K/HMPA/THF was stirred vigorously. The color of the solution changed to blue. The diphenylgermane solution was added dropwise and the change from blue to reddish brown usually appeared after about 40 min. The yield of diphenylgermylenedipotassium was determined from the concentration of diphenylgermane-$d_2$ after hydrolysis with $D_2O$ (84—96%).

*Preparation of Diphenylgermylenedilithium or Diphenylgermylenedisodium.* Diphenylgermylenedilithium or diphenylgermylenedisodium was prepared as described above diphenylgermylenedipotassium.

*Reaction of Diphenylgermylenedipotassium,* **1a**, *with Ethyl Bromide.* A typical example for the reactions of **1a** with organic halides was described. A solution of **1a** (0.534 mmol) in HMPA/THF was added to ethyl bromide (7.40 mmol) dissolved in THF (1.0 cm$^3$) and stirred for 30 min. The reaction vessel was cooled with water bath. After hydrolysis, the reaction mixture was extracted with ether. The organic layer was dried over anhydrous sodium sulfate.

*Reaction of* **1a** *with Acetophenone.* A typical example for the reactions of **1a** with carbonyl compounds was described. A solution of **1a** (0.527 mmol) in HMPA/THF was added to acetophenone (2.11 mmol) dissolved in THF (1.0 cm$^3$) and stirred for 30 min. The reaction vessel was cooled with water bath. After hydrolysis, the reaction mixture was extracted with ether. The organic layer was dried over anhydrous sodium sulfate.

*Reaction of KH with* p*-Bromotoluene.* A typical example for the reactions of KH with organic halides was described. KH(1.0 g, 24.9 mmol) was placed in the reaction vessel containing anhydrous HMPA (8.0 cm$^3$) and THF (16.0 cm$^3$) under argon. To this solution, *p*-bromotoluene (1.7 g, 10.0 mmol) was added and stirred for 30 min. The reaction vessel was cooled with water bath. After hydrolysis, the reaction mixture was extracted with ether. The organic layer was dried over anhydrous sodium sulfate.

*Reaction of KH with Acetone.* A typical example for the reactions of KH with carbonyl compounds was described. KH (1.0 g, 24.9 mmol) was placed in the reaction vessel containing anhydrous HMPA (8 cm$^3$) and THF (16 cm$^3$) under argon. To this solution, acetone (5.8 g, 0.10 mol) was added and stirred for 30 min. The reaction vessel was cooled with water bath. After hydrolysis, the organic layer was dried over anhydrous sodium sulfate.

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