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REACTIONS OF BIS(TRIETHYLGERMYL)CADMIUM WITH ALKYL HALIDES INVOLVING A ONE-ELECTRON TRANSFER PROCESS

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SUMMARY

The reactions of bis(triethylgermyl)cadmium with trityl chloride (chlorotriphenylmethane), benzyl bromide and allyl iodide in a 1/1 ratio in aprotic solvents proceed through the selective cleavage of the Ge–Cd–Ge linkage. As well as (triethylgermyl)cadmium halide, such reactions also yield the recombination products of Et_3Ge and R radicals (R = Ph_3C, $PhCH_2$, CH_2=$CHCH_2$, respectively). In addition, the reaction with trityl chloride gives free trityl radicals which may be detected by ESR spectroscopy.

INTRODUCTION

In a number of cases organometallic reagents are known to react with alkyl halides via an electron transfer process

$$RM + R'X \rightarrow MX + R^{\cdot} + R'^{\cdot}$$

Thus, the reaction of ethyllithium[1], phenylmagnesium bromide[2], divinylmercury[3], and some diarylmercury compounds[4] with trityl chloride have been found to occur via the generation of trityl radicals which may be detected by ESR spectroscopy. Recently this method has been used for detecting the radicals generated in the reaction of alkyl halides with alkyllithium reagents[5]. The formation of R and R' radicals in such reactions may also be deduced from the presence of the products of their coupling and disproportionation reactions in the reaction mixtures[6-8], or from their reactions with hydrogen donors (for example, with cumene[9]).

RESULTS AND DISCUSSION

We have shown that bis(triethylgermyl)cadmium reacts with trityl chloride in a 1/1 ratio in toluene to produce metallic cadmium (100% yield) and chlorotriethylgermane in 43% yield from the basis of eqns. (2) and (3). The other products were hexaethyldigermane (48%), triethyl(triphenylmethyl)germane (28%) and trityl radicals. The presence of trityl radicals was detected by ESR spectroscopy and by the formation of triphenylmethyl peroxide (46% yield) when the reaction mixture was exposed to atmospheric oxygen.

The reaction involves two distinct steps. The first step which is exothermic occurs immediately through the generation of trityl radicals, and it is only after this step has occurred that the deposition of metallic cadmium follows. This second step is completed after several days at room temperature (or for 2 h at 100°).

A reasonable assumption is that the first step involves an electron transfer from bis(triethylgermyl)cadmium to the trityl chloride as depicted by the scheme

$$Et_3GeCd{-}GeEt_3 + Ph_3CCl \rightarrow \begin{bmatrix} Et_3GeCd^+ \ {}^{\bullet}GeEt_3 \\ Cl^- \ {}^{\bullet}CPh_3 \end{bmatrix} \rightarrow$$

$$\rightarrow Et_3GeCdCl + Ph_3C^{\bullet} + Et_3Ge^{\bullet} \qquad (2)$$

$$Et_3Ge^{\bullet} + R^{\bullet} \rightarrow Et_3GeR \qquad (2a)$$

$$(R = Et_3Ge \text{ or } Ph_3C)$$

$$2\,Ph_3C^{\bullet} \rightleftarrows Ph_3C{-}CPh_3 \qquad (2b)$$

In the second step the decomposition of (triethylgermyl)cadmium chloride occurs, *viz.*,

$$Et_3GeCdCl \rightarrow Cd + Et_3GeCl \qquad (3)$$

That this reaction proceeds through a step-by-step cleavage of the Ge–Cd–Ge grouping with $Et_3GeCdCl$ present as an intermediate was readily confirmed. Thus, (triethylgermyl)cadmium bromide was obtained as a colourless solid by reacting equimolar amounts of bis(triethylgermyl)cadmium and ethyl bromide in hexane at room temperature. The other product of the reaction was tetraethylgermane.

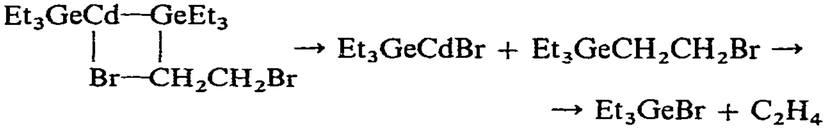
$$(Et_3Ge)_2Cd + EtBr \rightarrow Et_3GeCdBr + Et_4Ge \qquad (4)$$

Unlike (trialkylsilyl)-[10-13] and (trialkylgermyl)mercury halides[13,14], which decompose *in statu nascendi*, (triethylgermyl)cadmium bromide is reasonably stable. In hexane at 100° it decomposed after heating for ca. 2 h in a sealed evacuated tube. It is interesting, however, that $Et_3GeCdBr$ exhibited a marked decrease in stability in the presence of absolute methanol, when decomposition commenced even at room temperature. Irrespective of the decomposition temperature, metallic cadmium and bromotriethylgermane were always produced.

We have found that in the reaction of $Et_3GeCdBr$ with ethyl bromide in hexane the germanium–cadmium bond is also cleaved. However, this reaction only proceeded after heating the reactants at 100° for ca. 4 h.

$$Et_3GeCdBr + EtBr \rightarrow CdBr_2 + Et_4Ge \qquad (5)$$

On the other hand, the exothermic reaction of bis(triethylgermyl)cadmium with an equimolar amount of 1,2-dibromoethane occurred readily in hexane at ca. 20°, and resulted in a distinctively selective cleavage of the Ge–Cd–Ge linkage to give (triethylgermyl)cadmium bromide, bromotriethylgermane and ethylene. It may be assumed that in a similar fashion to the reactions depicted in eqns. (4) and (5) this reaction also proceeds via a four-centre mechanism without the presence of a free radical intermediate.



$$\begin{array}{l} Et_3GeCd{-}GeEt_3 \\ \quad\;\;| \quad\;\; | \\ \quad Br{-}CH_2CH_2Br \end{array} \rightarrow Et_3GeCdBr + Et_3GeCH_2CH_2Br \rightarrow$$

$$\rightarrow Et_3GeBr + C_2H_4 \qquad (6)$$

With benzyl bromide and allyl iodide, however, the selective cleavage of the Ge–Cd–Ge grouping in bis(triethylgermyl)cadmium proceeds via an electron-transfer mechanism. With benzyl bromide present in a 1/1 molar ratio, (triethylgermyl)-cadmium bromide, and bibenzyl and hexaethyldigermane, the recombination products of the radicals generated, were identified in the reaction mixture. With allyl iodide, the formation in low yields of biallyl and hexaethyldigermane during the reaction could be indicative of the intermediate formation of $CH_2{=}CHCH_2^{\bullet}$ and $Et_3Ge^{\bullet}$ radicals. The main products of this latter reaction were (triethylgermyl)-cadmium iodide and allyltriethylgermane.

We have also found that in reactions involving benzyl bromide and allyl iodide not only bis(triethylgermyl)cadmium, but also $Et_3GeCdBr$ (and Et_3GeCdI respectively) may act as electron donors. For example, the interaction of (triethylgermyl)-cadmium iodide with allyl iodide in hexane yielded CdI_2 and allyltriethylgermane, whilst biallyl and hexaethyldigermane were also identified (GLC) amongst the reaction products.

These examples indicate that the step-by-step cleavage of the Ge–Cd–Ge grouping by alkyl halides results in the transfer of a halogen atom to cadmium. This is in agreement with our previous findings[15] that the reaction of bis(triethylgermyl)-cadmium with excess ethyl bromide yields $CdBr_2$ and tetraethylgermane.

In contrast, the photochemical reactions of bis(triethylgermyl)mercury with ethyl bromide, benzyl bromide and bromobenzene[16,17] proceed through the normal fission of the Ge–Hg–Ge linkage in which germanium moieties become attached to bromine atoms *e.g.*:

$$(Et_3Ge)_2Hg + 2\,EtBr \xrightarrow{h\nu} Et_2Hg + 2\,Et_3GeBr \qquad (7)$$

Such a distinct difference in reaction routes might be explained by assuming that halogen addition occurs at the least electronegative atom. According to Batsanov[18] the electronegativities of cadmium, mercury and germanium are 1.7, 2.0 and 2.0, respectively, and hence in the Ge–Cd–Ge grouping of bis(triethylgermyl)cadmium the cadmium atom is the least electronegative, whereas in the Ge–Hg–Ge linkage of bis(triethylgermyl)mercury the halogen should add to germanium atom, thus accounting for the effect of the electron-releasing ethyl groups.

In agreement with this suggestion we have established that the reaction of trityl chloride with bis(triethylgermyl)mercury in toluene is very different from that described above for bis(triethylgermyl)cadmium. The main products of this reaction are mercury (93% yield), chlorotriethylgermane (68%) and hexaphenylethane (ca. 91%). No hexaethyldigermane or triethyl (triphenylmethyl)germane could be detected.

It is believed that the first step in this latter reaction is the formation of chlorotriethylgermane and of unstable bis(triphenylmethyl)mercury, the mercury compound being then decomposed to metallic mercury and trityl radicals, thus

$$(Et_3Ge)_2Hg + 2\,Ph_3CCl \rightarrow 2\,Et_3GeCl + (Ph_3C)_2Hg \rightarrow 2\,Ph_3C^{\bullet} + Hg \quad (8)$$

However, preliminary experiments have shown that in a similar fashion to its cadmium analogue bis(triethylgermyl)mercury can also behave as an electron donor. Thus, reaction of the mercury compound with tetracyanoethylene in benzene at 20° for 5–10 min yields a deep blue solution which produces and ESR spectrum corresponding to the tetracyanoethylene radical anion. In agreement with previously reported data[19], the spectrum contains 9 hyperfine components which result from the interaction of the unpaired electron with the four nitrogen atoms (^{14}N) of tetracyanoethylene (A_N 1.7±0.2 gauss). Initially the intensity of the resolved spectrum increases, but it then decreases and the characteristic hyperfine structure disappears. The final signal is that of a singlet ($\Delta U \simeq 8$ gauss) of weak intensity. The singlet signal was stable for several days in the absence of atmospheric oxygen.

Further investigations of this reaction are currently in progress.

EXPERIMENTAL

Reactions were carried out either in evacuated sealed ampoules or under an atmosphere of dry oxygen-free argon. Melting points were determined in the evacuated capillaries. GLC analyses were carried out using a "Tsvet-3" chromatograph with a heat conductivity detector. The columns used are described in the experimental details given below.

Reaction of $(Et_3Ge)_2Cd$ with trityl chloride

A solution of trityl chloride (4.4 g, 15.8 mmole) in 30 ml of anhydrous toluene was gradually added at room temperature to $(Et_3Ge)_2Cd$ (6.2 g, 14.4 mmole). An exothermal reaction was observed. Trityl radicals in the mixture were identified by ESR spectroscopy. The mixture was allowed to stand overnight at room temperature and then heated for 2 h at 100°. The organic layer was decanted from cadmium (1.6 g, 100%) and allowed to stand in air for 12 h at 20°. The solid which separated was recrystallized from chloroform to give triphenylmethyl peroxide (1.7 g, 46%), m.p. and mixed m.p. 178–180°.

Fractionation of the filtrate gave 1.2 g of chlorotriethylgermane (43%), b.p. 66–68°/20 mm, n_D^{20} 1.4640; and 1.1 g (48%) of hexaethyldigermane, b.p. 112–115°/2 mm, n_D^{20} 1.4920 (GLC identification), Triethyl(triphenylmethyl)germane (1.6 g, 28%) was also present, b.p. 210–215°/0.5 mm, n_D^{20} 1.5910 (lit.[20] b.p. 206–208°/0.23 mm, n_D^{20} 1.5915). No triethylgermane was detected (GLC).

Reaction of $(Et_3Ge)_2Cd$ with ethyl bromide

A mixture of ethyl bromide (3.1 g, 28.4 mmole) and $(Et_3Ge)_2Cd$ (2.2 g, 5.0 mmole) in 5 ml of hexane was kept overnight at room temperature. Volatile products were removed by trap-to-trap distillation *in vacuo* (pot temperature to 40°) into a receiver cooled with liquid nitrogen.

The crystalline residue was washed with cold hexane four times, and dried *in vacuo* at room temperature to give 1.5 g (86%) of $Et_3GeCdBr$ (decomposed on heating at 80–85°). (Found: Cd, 31.85. $C_6H_{15}BrCdGe$ calcd.: Cd, 31.92%.) Fractionation of the volatile products gave 0.84 g (88%) of tetraethylgermane, b.p. 60–62°/30 mm, n_D^{20} 1.4450, which was identified by comparison of its GLC retention time with that of an authentic sample.

Reaction of $Et_3GeCdBr$ with ethyl bromide

A solution of ethyl bromide (2.3 g, 21.1 mmole) in 5 ml of hexane was added to $Et_3GeCdBr$ (1.4 g, 3.2 mmole). The mixture was heated for 4 h at 100°. The organic layer was decanted from $CdBr_2$ (0.88 g, 81%) and fractionated to give 0.58 g (77.3%) of tetraethylgermane, b.p. 60–61°/30 mm, n_D^{20} 1.4440.

Reaction of $(Et_3Ge)_2Cd$ with 1,2-dibromoethane

To a precooled (−70°) solution of 1,2-dibromoethane (1.0 g, 5.3 mmole) in 10 ml of hexane $(Et_3Ge)_2Cd$ (2.5 g, 5.7 mmole) was added. On warming to room temperature, an exothermic reaction accompanied by ethylene evolution (120 ml, 98%) was observed. The organic layer was decanted from the crystalline product and fractionally distilled to give bromotriethylgermane (1.2 g, 85%), b.p. 65–68°/10 mm, n_D^{20} 1.4830. The compound was characterized by its GLC retention time.

The crystalline solid was washed with hexane and dried *in vacuo* to give 1.8 g (89%) of $Et_3GeCdBr$, m.p. 80–83° (decomp.). (Found: Cd, 31.60. $C_6H_{15}BrCdGe$ calcd.: Cd, 31.92%.)

Reaction of $Et_3GeCdBr$ with 1,2-dibromoethane

Under the same conditions as that of the previous run, a mixture of $Et_3GeCdBr$ (2.3 g, 6.5 mmole) and 1,2-dibromoethane (2.5 g, 13.2 mmole) in 5 ml of hexane yielded ethylene (125 ml, 86%), $CdBr_2$ (1.5 g, 88%) and bromotriethylgermane (1.1 g, 73%), b.p. 65–68°/10 mm, n_D^{20} 1.4855.

Decomposition of $Et_3GeCdBr$ in hexane

A mixture of $Et_3GeCdBr$ (2.2 g, 6.2 mmole) and hexane (5 ml) was held in a sealed evacuated tube for 2 h at 100°. The organic layer was decanted from the residual cadmium (0.64 g, 91%) and fractionated. 1.06 g (71%) of bromotriethylgermane was obtained, b.p. 64–67°/9 mm, n_D^{20} 1.4820.

Reaction of $(Et_3Ge)_2Cd$ with benzyl bromide

A mixture of $(Et_3Ge)_2Cd$ (4.88 g, 11.2 mmole) and benzyl bromide (2.02 g, 11.8 mmole) in 10 ml of hexane was allowed to stand at room temperature for 2 h. The usual work-up gave $Et_3GeCdBr$ (3.5 g, 89%), m.p. 81–84° (decomp.). (Found: Cd, 31.55. $C_6H_{15}BrCdGe$ calcd.: Cd, 31.92%.) From the hexane solution a fraction with b.p. 105–120°/2 mm was isolated. This fraction was shown by GLC analyses to contain hexaethyldigermane (about 1.1 g, 60%) and bibenzyl (0.5 g, 49%) (0.3 × 100 cm column; 15% PEG 20M on Airosyl at a 35 ml/min He flow rate with the temperature held at 170°).

Reaction of $Et_3GeCdBr$ with benzyl bromide

A mixture of $Et_3GeCdBr$ (2.5 g, 7.1 mmole) and benzyl bromide (1.2 g, 7.0 mmole) in 6 ml benzene was heated for 3 h at 70–80°. The organic layer was decanted from $CdBr_2$ (1.38 g, 71%) and fractionated. A fraction with b.p. 105–120°/2 mm was analyzed by GLC. The only products observed were hexaethyldigermane (0.7 g, 62%) and bibenzyl (0.6 g, 92%).

Reaction of $(Et_3Ge)_2Cd$ with allyl iodide

To an anhydrous solution of allyl iodide (2.1 g, 12.5 mmole) in 10 ml of hexane, frozen in an evacuated ampoule cooled with liquid nitrogen, 5.2 g (12.0 mmole) of $(Et_3Ge)_2Cd$ was added. The mixture was allowed to melt. The resulting exothermic reaction was complete at ca. 20°. In the usual way Et_3GeCdI (4.5 g, 93%) was isolated, decomp. 65°. (Found: Cd, 28.57. $C_6H_{15}CdGeI$ calcd.: Cd, 28.16%.)

The liquid part of the reaction mixture was fractionated to give 1.7 g of allyltriethylgermane (70%), b.p. 50–52°/10 mm, n_D^{20} 1.4570 (lit.[21] b.p. 180°/732 mm, n_D^{20} 1.4594). The infrared spectrum of this compound was in agreement with that previously reported[22].

In a separate experiment, the liquid part of the mixture was analyzed by GLC methods (column 100 × 0.3 cm consisting of 20% Apiezon L on Chromosorb W at 70° at a flow rate of 20 ml/min of He). Allyltriethylgermane, together with hexaethyldigermane (20%) and biallyl (23%), were detected in the mixture.

Reaction of Et_3GeCdI with allyl iodide

Addition of Et_3GeCdI (3.4 g, 8.5 mmole) to a solution of allyl iodide (1.4 g, 8.3 mmole) in 10 ml of benzene, in a similar manner to that described for the previous experiment, gave CdI_2 (3.0 g, 100%), allyltriethylgermane (1.2 g, 76%), b.p. 51–53°/10 mm, n_D^{20} 1.4610, and traces of hexaethyldigermane and biallyl.

Reaction of $(Et_3Ge)_2Hg$ with trityl chloride

A solution of trityl chloride (3.8 g, 13.6 mmole) in 15 ml of toluene was added to $(Et_3Ge)_2Hg$ (3.6 g, 6.9 mmole). After 15–20 min a weak exothermal reaction occurred resulting in the precipitation of metallic mercury (1.3 g, 94%). On cooling the organic layer to −40° (12 h), hexaphenylethane crystallized out. It was collected and washed with small volumes of cold toluene, yielding 3.2 g, of a crude product (95%). Recrystallization of this product from toluene gave hexaphenylethane, m.p. 143–146° (decomp.).

Fractional distillation of the combined mother liquor and toluene washings yielded chlorotriethylgermane (1.8 g, 68%), b.p. 64–66°/20 mm, n_D^{20} 1.4621. Identification was made on the basis of the GLC retention time.

The crude hexaphenylethane isolated (1.3 g, 2.6 mmole) was dissolved in 10 ml of benzene and allowed to stand overnight in air. Triphenylmethyl peroxide (1.1 g, 81%) was isolated in the usual manner, m.p. 179–180° (mixed m.p.).

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