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ORGANOGERMANIUM COMPOUNDS

XI*. THE STEREOCHEMISTRY OF THE REACTIONS OF OPTICALLY ACTIVE ETHYL(1-NAPHTHYL)PHENYLGERMYLLITHIUM WITH SOME CARBONYL COMPOUNDS

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SUMMARY

Optically active (*R*)-ethyl(1-naphthyl)phenylgermyllithium, R'_3Ge^*Li, is obtained in ethereal solution by treatment of the hydride (*R*)-(+)-R'_3GeH with n-butyllithium. Its reactions with water [to give (+)-R'_3GeH], carbon dioxide [to give (−)-R_3GeCO_2H], benzophenone [to give (−)-$R_3GeC(OH)Ph_2$], 2-methylcyclohexanone [to give (−)-$R'_3Ge\overline{C(OH)CHMe(CH_2)_3CH_2}$] and paraformaldehyde [to give (+)-R'_3GeCH_2OH] are all thought to proceed with retention of configuration at the germanium atom.

The acid (−)-$R'_3GeCOOH$ undergoes Ge–C bond cleavage when treated with n-butyllithium, to give R'_3Ge^*Li, and 90% overall retention of configuration is found in the optical cycle (+)-$R'_3GeH \rightarrow R'_3Ge^*Li \rightarrow$ (−)-$R'_3GeCO_2H \rightarrow R'_3Ge^*Li \rightarrow$ (+)-R_3GeH. Reduction of the acid with lithium aluminium hydride gives the racemic alcohol, (±)-R'_3GeCH_2OH.

INTRODUCTION

We have previously described studies of the stereochemistry of nucleophilic substitutions at germanium in $Et(1\text{-}C_{10}H_7)PhGeX$ (R'_3GeX) compounds[1], and now discuss the stereochemistry of the reactions of the optically active lithium derivative, R'_3Ge^*Li, with some carbonyl compounds**. The study and the conclusions are mainly very similar to those reached by Brook and Peddle in their work on the closely related reagent $Me(1\text{-}C_{10}H_7)PhGe^*Li$[3].

RESULTS AND DISCUSSION

The germyl-lithium compound R'_3Ge^*Li is readily obtained as a red solution

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* For Part X see ref. 1.

** For a preliminary report see ref. 2. The asterisk in R'_3Ge^*Li denotes that the reagent was optically active although its rotation was not measured.

TABLE 1

REACTIONS OF R'_3Ge^*Li WITH WATER AND CARBONYL COMPOUNDS

$[\alpha]_D^{25}$ (°) *of* R'_3GeH	*Reagent*	*Product, with* $[\alpha]_D^{25}$ (°)	*Predominant stereochemistry*
+22.6	H_2O	$(+)\text{-}R'_3GeH$, +17.8	Ret.
+22.0	CO_2	$(-)\text{-}R'_3GeCO_2H$, −9.5	Ret.
+20.0[a]	$Ph_2C{=}O$	$(-)\text{-}R'_3GeC(OH)Ph_2$, −15.2	Ret.
+13.0	2-Methylcyclohexanone	$(-)\text{-}R'_3Ge\overline{C(OH)CHMe(CH_2)_3CH_2}$, −6.8	Ret.
+13.0	(*para*) HCHO	$(+)\text{-}R'_3GeCH_2OH$, +1.1	Ret.

[a] Erroneously reported as +13.0 in ref. 2.

by treatment of the hydride $(+)\text{-}R'_3GeH$ with n-butyllithium in ether. From our results it is clear that the germyllithium reagent is quite optically stable in solution.

The results of some of the reactions of R'_3Ge^*Li are shown in Table 1. Treatment of the solution with water regenerates $(+)\text{-}R'_3GeH$, to establish the Walden cycle (1). This cycle involves overall retention of configuration with 89% stereospecificity, rather similar to the stereospecificity observed for the same cycle with $Me(1\text{-}C_{10}H_7)PhGe^*Li$[3]. With Brook and his colleagues[3,4], we believe that retention is involved in both steps of the cycle.

$$\begin{array}{lll} & (+)\text{-}R'_3GeH + n\text{-}BuLi \rightarrow R'_3Ge^*Li \xrightarrow{H_2O} (+)\text{-}R'_3GeH & \qquad (1)\\ [\alpha]_D & +22.6^\circ \qquad\qquad\qquad\qquad\qquad\qquad\quad +17.8^\circ & \end{array}$$

The reaction with carbon dioxide, followed by hydrolysis, gives the acid $(-)\text{-}R'_3GeCO_2H$ in good yield. Application of Brewster's Rules (*cf.* ref. 1) indicates that $(-)\text{-}R'_3GeCO_2H$ has the same configuration as $(+)\text{-}R'_3GeH$, (which is known to have the *R*-configuration[5]) and so the reaction of the R'_3Ge^*Li with carbon dioxide also involves retention of configuration at germanium.

In a reaction of a type previously unobserved, the acid was found to regenerate R'_3Ge^*Li when treated with n-butyllithium in ether, and thus a four-step Walden cycle (2) was established.

$$\begin{tikzcd}
 & (+)\text{-}R'_3GeH \arrow[r, "n\text{-}BuLi"] & R'_3Ge^*Li \arrow[r, "(i)\ CO_2", "(ii)\ H_2O"'] & (-)\text{-}R'_3GeCO_2H \\
{[\alpha]_D} & +21.5^\circ & & -9.5^\circ \arrow[d, "n\text{-}BuLi"] \\
 & (+)\text{-}R'_3GeH & & R'_3Ge^*Li \arrow[ll] \\
{[\alpha]_D} & +17.8^\circ & &
\end{tikzcd} \qquad (2)$$

This cycle involves retention, with 91% overall stereospecificity, and since effectively the same stereospecificity was found for simple formation and hydrolysis of R'_3Ge^*Li in cycle (1), it is clear that the conversion of R'_3Ge^*Li to $(-)\text{-}R'_3GeCO_2H$ and the cleavage of the latter with n-butyllithium must both be highly stereospecific. It seems safe to assume that the formation of $(-)\text{-}R'_3GeCOOH$ from R'_3Ge^*Li involves retention of configuration (*cf.* ref. 3), and it follows that the cleavage of $(-)\text{-}R'_3GeCO_2H$ by n-butyllithium also involves retention.

Hydrolysis of the mixture obtained from $(-)\text{-}R'_3GeCO_2H$ and n-butyllithium gave, in addition to $(+)\text{-}R'_3GeH$ (which was isolated in 40% yield), di-n-butyl ketone (in about 20% yield) and an unidentified germanium-containing product with a relatively large negative specific rotation; the approximate ratios of the three products, estimated roughly from GLC and IR peak heights, were 2/1/2. The di-n-butyl ketone is probably formed after the cleavage, by sequence (*i*) or (*ii*), and we confirmed that di-n-butyl ketone was formed almost exclusively when carbon dioxide was bubbled into a solution of n-butyllithium.

(*i*). $$R'_3GeCO_2H + n\text{-BuLi} \rightarrow R'_3GeLi + CO_2 + n\text{-BuH}$$
$$CO_2 + n\text{-BuLi} \rightarrow n\text{-Bu}_2C(OLi)_2 \xrightarrow{H_2O} n\text{-Bu}_2CO$$

(*ii*). $$R'_3GeCO_2H + n\text{-BuLi} \rightarrow R'_3GeCOOLi + n\text{-BuH}$$
$$R'_3GeCO_2Li + n\text{-BuLi} \rightarrow R'_3GeLi + n\text{-BuCO}_2Li$$
$$n\text{-BuCO}_2Li + n\text{-BuLi} \rightarrow n\text{-Bu}_2C(OLi)_2 \xrightarrow{H_2O} n\text{-Bu}_2CO$$

The unidentified product may possibly have been one of the carbinols $(R'_3Ge)_x(n\text{-}Bu)_{3-x}COH$ $(x=1\text{–}3)$.

Conversion of the acid $(-)\text{-}R'_3GeCO_2H$ into the ester $(-)\text{-}R'_3GeCOOMe$ and hence into the alkoxide $(+)\text{-}R'_3GeOMe$, which was then reduced to $(+)\text{-}R'_3GeH$, enabled the 5-step Walden cycle (3) to be established.

$$\begin{tikzcd}
 & (+)\text{-}R'_3GeH \arrow[r, "n\text{-BuLi}"] & R'_3Ge^*Li \arrow[r, "CO_2"] & (-)\text{-}R'_3GeCO_2H & \\
{[\alpha]_D} & +21.0^\circ & & -9.8^\circ \arrow[d, "CH_2N_2"] & (3) \\
 & (+)\text{-}R'_3GeH & (+)\text{-}R'_3GeOMe \arrow[l, "LiAlH_4"'] & (-)\text{-}R'_3GeCO_2Me \arrow[l, "heat"'] & \\
{[\alpha]_D} & +8.2^\circ & +5.9^\circ & -5.6^\circ &
\end{tikzcd}$$

In this cycle there is 70% retention of configuration overall at germanium; the third step must proceed with retention since the germanium atom is not involved, and the last step clearly involves retention (*cf.* ref. 1). Thus if, as we believe, the first and second steps both involve retention, the fourth step, involving the thermal conversion of $(-)\text{-}R'_3GeCO_2Me$ to $(+)\text{-}R'_3GeOMe$ must also involve retention, as required by the mechanism for this type of reaction proposed by Brook[6]. (Rather similar reasoning was applied by Brook and Peddle in analysing the exactly parallel reactions involving $Me(1\text{-}C_{10}H_7)PhGeX$ compounds[3].) Every step in cycle (3) is thus thought to involve retention. The corresponding cycle from $(+)\text{-}Me(1\text{-}C_{10}H_7)PhGeH$ had a somewhat higher overall stereospecificity[3]; we suspect that the main loss of optical activity in our cycle (3) occurs in the (relatively slow) reduction of the $(-)\text{-}R'_3GeOMe$ to the hydride, since the latter is known to undergo racemization slowly in ether, and more rapidly when lithium aluminium hydride is present[7].

The reaction of R'_3Ge^*Li with benzophenone gives the expected carbinol $(-)\text{-}R'_3GeC(OH)Ph_2$ (see Table 1), and by analogy with Brook and Peddle's system[3], we can confidently conclude that the reaction involves retention of configuration at germanium. The reaction with 2-methylcyclohexanone to give the expected carbinol (Table 1) no doubt also involves retention.

The optically-active carbinol $(+)\text{-}R'_3GeCH_2OH$, with a rather low optical purity, was obtained from the interaction of the lithium compound with paraformaldehyde, as in eqn. (4).

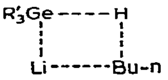
$$\begin{array}{lllll} & (+)\text{-}R_3GeH \longrightarrow & R'_3Ge^*Li \xrightarrow[(ii)\,H_2O]{(i)\,HCHO} & R'_3GeCH_2OH & \quad (4) \\ [\alpha]_D & +13.0^\circ & & +1.1^\circ & \end{array}$$

The same carbinol was obtained by treatment of the ester $(-)\text{-}R'_3GeCO_2GeR'_3$ [prepared from $(+)\text{-}R'_3GeH$ having $[\alpha]_D = +22.0^\circ$] with lithium aluminium hydride, as in eqn. (5).

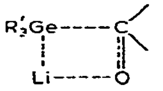
$$\begin{array}{lllll} & (-)\text{-}R'_3GeCO_2GeR'_3 + LiAlH_4 \longrightarrow & (+)\text{-}R'_3GeCH_2OH + & (-)\text{-}R'_3GeH & \quad (5) \\ [\alpha]_D & -10.0^\circ & +2.0^\circ & -2.8^\circ & \end{array}$$

However, reduction of the acid $(-)\text{-}R'_3GeCO_2H$ with lithium aluminium hydride gave, in good yield, the inactive carbinol, $(\pm)\text{-}R'_3GeCH_2OH$, along with small amounts of inactive $(\pm)\text{-}R'_3GeH$. Since $(\pm)\text{-}R'_3GeCH_2OH$ was found not to undergo racemization under the reaction conditions, the loss of activity in the reduction of $(-)\text{-}R'_3Ge\text{-}CO_2H$ either occurs during the reduction itself, or, more probably, by racemization of the acid or its salt before reduction.

The formation of R'_3GeLi from the hydride or from the acid $(-)\text{-}R'_3GeCO_2H$, and all reactions of R'_3Ge^*Li examined appear to involve retention of configuration at germanium, and it is very likely that four-centre processes such as (I)–(III) are operative



(I)



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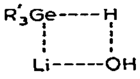

(III)

EXPERIMENTAL

General

Solvents were dried as previously described[1]. Rotations were measured in benzene.

Preparation and hydrolysis of R'_3Ge^*Li

(*i*). In a typical preparation, $(+)\text{-}R'_3GeH$ (102 mg, 0.33 mmole), $[\alpha]_D$ 22.6°, was added under dry nitrogen to n-butyllithium (0.40 mmole) in diethyl ether which had been freshly distilled under nitrogen from lithium aluminium hydride. The mixture was refluxed gently under dry nitrogen for 30 min, to give a clear deep reddish-brown solution.

(*ii*). The above solution was shaken, initially cautiously then vigorously, with water (20 ml) for 5 min, and the ethereal layer was separated and evaporated to dryness. The product was eluted in carbon tetrachloride through a silica gel column and recovered to give $(+)\text{-}R'_3GeH$ (82 mg, 80%), $[\alpha]_D$ +17.8°.

Reactions with ketones

(*i*). Benzophenone (60 mg, 0.30 mmole) was added with swirling to a solution of R'_3Ge^*Li (0.30 mmole) prepared in ether (25 ml) from (+)-R'_3GeH, $[\alpha]_D$ +20.0°. After 4 h at room temperature, during which the red colour had almost disappeared, the mixture was added to 0.1 *M* hydrochloric acid. Ether extraction followed by washing, drying ($MgSO_4$), and removal of volatile material by gentle heating under reduced pressure, left (−)-[ethyl(1-naphyl)phenylgermyl]diphenylmethanol (155 mg, 95%), $[\alpha]_D$ −14.2° (*c*, 7.7) as a viscous gum which could not be crystallized. Its IR spectrum was identical with that of the racemic material, which was obtained as described under (*ii*).

(*ii*). The procedure described under (*i*) was repeated starting from (±)-R'_3GeH. The gum obtained was eluted in benzene through a column of neutral alumina (0.3 m × 0.5 cm; Woelm, Activity Grade 1) to give (±)-[ethyl(1-naphthyl)phenylgermyl]-diphenylmethanol (60 mg, 20%) as a crystalline solid, m.p. 53–57°. (Found: C, 75.6; H, 5.9. $C_{31}H_{28}OGe$ calcd.: C, 76.1; H, 5.8%.) The IR spectrum had the expected characteristics.

(*iii*). 2-Methylcyclohexanone (60 mg, 0.50 mmole) was added to a solution of R'_3Ge^*Li (0.3 mmole) prepared in ether (25 ml) from (+)-R'_3GeH, $[\alpha]_D$ +13.0°. After 30 min the ether was removed and the residue was extracted with hexane. Filtration, followed by evaporation of the solvent gave a clear oil, which was heated at 120°/0.2 mm to remove any unchanged 2-methylcyclohexanone. The oil was distilled to give (−)-1-[ethyl(1-naphthyl)phenylgermyl]-2-methylcyclohexanol (96 mg, 60%), n_D^{25} 1.6230, $[\alpha]_D$ −6.8° (*c*, 4.8). (Found: C, 71.4; H, 7.2. $C_{25}H_{29}GeO$ calcd.: C, 71.8; H, 7.0%.) The IR spectrum had the expected characteristics.

Preparation of (−)-R'_3GeCO_2H

A fast stream of carbon dioxide was passed into a solution of R'_3Ge^*Li (1.5 mmole) prepared in ether (25 ml) from (+)-R'_3GeH, $[\alpha]_D$ +22.0°. After 1 min, during which the red colour had been discharged, the ether was removed to leave a solid. This was taken up in 0.5 *M* aqueous sodium hydroxide, and the solution was extracted several times with ether. The aqueous solution was acidified with hydrochloric acid and quickly extracted with ether. The ethereal extract was washed, dried ($MgSO_4$) and evaporated to leave a gum, which was recrystallized from cyclohexane to give (−)-ethyl(1-naphthyl)phenylgermanecarboxylic acid (480 mg, 80%), m.p. 120–124°, $[\alpha]_D$ −9.5° (*c*, 7.2). (Found: C, 65.1; H, 5.1. $C_{19}H_{18}O_2Ge$ calcd.: C, 65.0; H, 5.15%.) In addition to the R'_3Ge peaks, the IR spectrum in Nujol showed an intense absorption at 3600–2400 cm^{-1}, an intense carbonyl band at 1650 cm^{-1}, and a strong band at 1210 cm^{-1}.

Reaction of (−)-R'_3GeCO_2H with lithium aluminium hydride

(*i*). A mixture of (−)-R'_3GeCO_2H (120 mg, 0.30 mmole) and a large excess of lithium aluminium hydride in ether was refluxed for 30 min. Acetone was cautiously added with ice-cooling, and the mixture was added to 0.1 *M* hydrochloric acid. Ether extraction followed by washing, drying ($MgSO_4$), and evaporation of the extract left an oil, which was distilled to give virtually racemic [ethyl(1-napthyl)phenylgermyl]-methanol (90 mg, 70%), n_D^{25} 1.6529, $[\alpha]_D$ −0.4° (*c*, 3.5), having an IR spectrum identical with that of an authentic sample prepared as described below.

(*ii*). A mixture of (−)-R'_3GeCO_2H (480 mg, 1.2 mmole), $[\alpha]_D$ −9.8°, and a large excess of lithium aluminium hydride in ether was refluxed for 1 h. Working-up as in (*i*) initially gave an oil which was eluted with chloroform through a column of silica gel. The first 50 mg of material recovered from the column was identified from its IR spectrum as (±)-R'_3GeH. The remaining product was shown by GLC, IR spectroscopy, and elemental analysis to be almost pure R'_3GeCH_2OH, $[\alpha]_D$ +0.3°.

Preparation of (+)-*[ethyl(1-naphthyl)phenylgermyl]methanol*

A large excess of paraformaldehyde was added with swirling to a solution of R'_3Ge^*Li prepared in ether (30 ml) from (+)-R'_3GeH (130 mg, 0.40 mmole), $[\alpha]_D$ +13.0°. After 10 min, the mixture was filtered and the ether was removed from the filtrate. The residual oil was heated at 60°/0.2 mm to remove volatile material, and distilled to give (+)-[ethyl(1-naphthyl)phenylgermyl]methanol (nc), n_D^{25} 1.6550, $[\alpha]_D$ +1.1 (*c*, 4.5). (Found: C, 67.4; H, 5.9. $C_{19}H_{20}GeO$ calcd.: C, 67.7; H, 6.0%.) The IR spectrum had the expected characteristics.

The specific rotation of the product was unchanged when a sample was kept at 150° for 20 min or refluxed with lithium aluminium hydride in ether for 30 min.

Reaction of (−)-R'_3GeCO_2H *with n-butyllithium*

When n-butyllithium (20 mmole of a 1.6 *M* solution in hexane) was added to a solution of (−)-R'_3GeCO_2H (420 mg, 1.2 mmole), $[\alpha]_D$ −9.8°, in ether the mixture became deep orange-brown almost immediately and a precipitate formed. The mixture was refluxed for 30 min, then added to 0.1 *M* HCl. Ether extraction, followed by washing, drying ($MgSO_4$) and evaporation of the extract left an oil (316 mg), $[\alpha]_D$ −3.0°, the IR spectrum of which showed a Ge–H band at 2020 cm^{-1} and a carbonyl band at 1710 cm^{-1}, but no bands at 3600–2400 cm^{-1} (OH) and 1650 cm^{-1} (carbonyl) associated with the original acid. When this oil was kept at 120° at 0.2 mm for 20 min it lost 20% of its weight, its original fruity smell disappeared, and the carbonyl band disappeared from the IR spectrum. The evolved liquid, collected in a cold trap, had an IR spectrum identical with that of an authentic sample of di-n-butyl ketone, so it was concluded that this compound constituted about 20% of the products. The oil was eluted in benzene through a column of neutral alumina (0.3 m × 0.5 cm; Woelm, Activity Grade 1). The first fraction (60 mg, 40%) was identified by its IR spectrum as (+)-R'_3GeH, $[\alpha]_D$ +16.8° (*c*, 3.0). Much later an oil (26 mg, 26%) having $[\alpha]_D$ −15.5° (*c*, 1.3) was eluted; its IR spectrum showed, in addition to the usual R'_3Ge bonds, an absorption at 3400–3600 cm^{-1}.

When the above procedure was repeated starting from (±)-R'_3GeH but with a reaction time of only 2 min at 0°, virtually identical results were obtained. GLC analysis of the mixture left after removal of the di-n-butyl ketone showed that it contained only two major products, present in comparable amounts, one being R'_3GeH and the other having a much longer retention time.

Reaction of n-butyllithium with carbon dioxide

A rapid stream of carbon dioxide was passed into a solution of n-butyllithium (0.8 mmole) in ether. After 2 min the ether was carefully removed and the remaining liquid distilled to give di-n-butyl ketone, which was identified by comparison of its IR spectrum and GLC retention time with those of an authentic sample.

Preparation and thermal decomposition of (−)-R'_3GeCO_2Me

(*i*). A solution of (−)-R'_3GeCO_2H (500 mg, 1.4 mmole), $[\alpha]_D$ −9.1°, in ether (25 ml) was treated with diazomethane[8]. Residual diazomethane was destroyed by careful addition of dilute acetic acid, and the mixture was added to 0.1 *M* hydrochloric acid. Ether extraction, followed by washing, drying ($MgSO_4$), and evaporation of the extract left an oil, which was eluted with chloroform through a column (0.3 m × 0.5 cm) of chromatographic silica gel to give (−)-[methyl ethyl(1-naphthyl)phenylgermanecarboxylate] (nc) (387 mg, 75%), n_D^{25} 1.6545, $[\alpha]_D$ −5.4° (*c*, 19.3) (Found: C, 65.5; H, 5.6. $C_{20}H_{20}O_2Ge$ calcd.: C, 65.8; H, 5.5%.) In addition to the usual R'_3Ge bands the IR spectrum showed strong absorptions at 1690 (C=O) and 1130 cm^{-1}.

(*ii*). A sample of (−)-R'_3GeCO_2Me (170 mg, 0.50 mmole) $[\alpha]_D$ −5.4°, was kept at 270° for 15 min, after which no more bubbles of gas could be seen emerging from the oil. Comparison of the IR spectrum of the viscous residue with that of an authentic sample of racemic material showed it was (+)-ethyl(methoxy)(1-naphthyl)-phenylgermane (147 mg, 97%), $[\alpha]_D$ +5.9° (*c*, 7.3). No attempt was made to crystallize this material, which was reduced with lithium aluminium hydride (see ref. 1) to give (+)-R'_3GeH, $[\alpha]_D$ +8.2°.

When the thermal decomposition was repeated with (±)-R'_3GeCO_2Me, the (±)-R'_3GeOMe produced was crystallized from pentane to give a solid of m.p. 74–77°.

Preparation and reduction of (−)-$R'_3GeCO_2GeR'_3$-(−).

(*i*). A sample of (−)-R'_3GeCO_2H (182 mg, 0.50 mmole), $[\alpha]_D$ −9.1°, was kept at 200° for 10 min, after which no more bubbles emerged from the liquid. The residual pale yellow oil (170 mg, 95%), $[\alpha]_D$ −9.8° (*c*, 8.5), was identified as (−)-ethyl(1-naphthyl)phenylgermyl (−)-ethyl(1-naphthyl)phenylgermanecarboxylate by comparison of its IR spectra with that of an authentic sample of the racemic compound.

(*ii*). A mixture of (−)-$R'_3GeCO_2GeR'_3$-(−) (250 mg, 0.40 mmole), $[\alpha]_D$ −10.0°, and lithium aluminium hydride (400 mg, 1.0 mmole) in ether (30 ml) was refluxed for 30 min. Acetic acid was cautiously added with cooling, and the mixture was then poured into 0.1 *M* hydrochloric acid. Ether extraction, followed by washing, drying, and removal of volatile material under reduced pressure left an oil (173 mg), $[\alpha]_D$ −0.9° (*c*, 8.6). This was eluted in chloroform through a 0.3 m × 0.5 cm column of chromatographic silica gel. The first fraction was (−)-R'_3GeH, (80 mg, 35%), $[\alpha]_D$ −2.8° (*c*, 2.5), having an IR spectrum identical with that of an authentic sample. The second fraction, which came off the column much later, was (−)-R'_3GeCH_2OH, (85 mg, 40%), n_D^{25} 1.6510, $[\alpha]_D$ +2.0° (*c*, 2.1), having an IR spectrum identical with that of an authentic sample.

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