

8 g. of diphenyl ketene in 110 ml. of pentane at 0° for 4.5 hours. The solution was filtered and the collected solid washed with petroleum ether. This solid, weighing 5 g., was triturated with a solution of 12 ml. of acetone and 20 ml. of ether. The undissolved solid was dissolved in benzene and the resulting solution extracted with 10% sodium carbonate. The benzene solution was washed with water, dried over magnesium sulfate, and the benzene evaporated. The residual solid was Staudinger's "high molecular weight" polyester of benzoic acid. The "low molecular weight" polyester was obtained from the ether-acetone wash. The infrared spectra of the "high" and "low" polymers were identical with the spectrum of the polymer from the decomposition of permalonate. The gross physical properties of all these polymers, e.g., the wide melting point range, the change in form on trituration with various solvents and the solubility in various solvents, were quite similar. No molecular weight measurements were made, but the average molecular weight of the polymer obtained from perester is probably between the molecular weights of the "high" and "low" polymers from the oxygenation of diphenyl ketene.

**Reaction with Methanol.**—Di-*tert*-butylperoxy diphenylmalonate (102 mg., 0.255 mmole) was dissolved in 2 ml. of methanol, and the resulting solution degassed, sealed under vacuum, and heated for 2.5 hours at 60°

When decomposition was complete the solvent and volatile products were distilled from the reaction solution, leaving a residue of 41.9 mg. The infrared spectrum was almost identical with that of  $\alpha$ -methoxydiphenylacetic acid. The only difference was a weak band at 6.01  $\mu$  which can be attributed to a trace of benzophenone. Chromatographing the residue on silica gel neither changed the spectrum nor yielded any new compounds. Assuming that 40 mg. of the residue was the  $\alpha$ -methoxy acid, this would correspond to a 65% conversion from perester.

$\alpha$ -Methoxydiphenylacetic acid for comparison purposes was prepared using the method described by Klosa.<sup>23</sup> Recrystallization from benzene-petroleum ether yielded white crystals melting at 105–106.5° (reported m.p. 104–106°).

The 1,1,2-triphenyl-2-methylpropane, previously unknown, was identified by its infrared spectrum and its analysis. This compound was recrystallized from ethanol-water; m.p. 70.2–70.8°.

*Anal.* Calcd. for C<sub>22</sub>H<sub>22</sub>: C, 92.26; H, 7.74. Found: C, 92.10; H, 7.87.

**Acknowledgment.**—We thank the National Institutes of Health for support of this work.

(23) J. Klosa, *Archiv. Pharm.*, **288**, 42 (1955).

## COMMUNICATIONS TO THE EDITOR

### Resolution of an Asymmetric Organogermanium Compound, Methyl- $\alpha$ -naphthylphenylgermane

Sir:

To the best of our knowledge the resolution of an organogermanium compound asymmetric at germanium has not been reported, although Schwarz and Lewinsohn<sup>1</sup> have reported attempts to resolve isopropylphenylethylbromogermane through the  $\alpha$ -bromo- $\pi$ -camphor sulfonate ester. We therefore wish to report the first resolution of an asymmetric germanium compound into its enantiomers, namely, the compound methyl- $\alpha$ -naphthylphenylgermane (I).<sup>1a</sup> This compound is of particular interest since it is isostructural with methyl- $\alpha$ -naphthylphenylsilane, the absolute configuration of which has recently been reported.<sup>2</sup> In addition, considerable knowledge regarding the stereochemistry of displacements at silicon has been derived from the study of the reactions of this compound and its derivatives.<sup>3–6</sup>

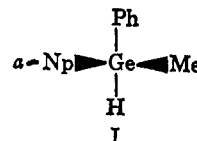
The synthesis and resolution of methyl- $\alpha$ -naphthylphenylgermane was best accomplished by the route shown in Fig. 1. This route, utilizing the ready cleavage of phenyl groups from germanium by bromine,<sup>1,7</sup> was far superior to that using germanium tetrachloride and successive couplings with the appropriate Grignard reagents.

Several details of this synthetic route warrant comment. The methyl- $\alpha$ -naphthylphenylbromogermane derived from coupling of  $\alpha$ -naphthyl Grignard reagent with methylphenyldibromogermane was not isolated, but the entire reaction mixture was reduced to the germane in order to facilitate purification at this stage. The subsequent bromination was best accomplished using N-bromosuccinimide since bromine

was found to lead to considerable cleavage of the naphthyl group from germanium.

The resolution was achieved by converting the bromogermane to the methoxygermane, which was not isolated because of its anticipated instability<sup>8</sup> but was instead immediately converted to the menthoxygermane by exchange with (–)menthol. This compound in pentane yielded a crystalline diastereomer,  $[\alpha]^{22D} - 49.3^\circ$ , which on treatment with lithium aluminum hydride gave crystalline methyl- $\alpha$ -naphthylphenylgermane,  $[\alpha]^{26D} + 26.7^\circ$ . Following removal of several crops of this diastereomer, the residual oil,  $[\alpha]^{20D} - 59.4^\circ$ , was similarly reduced to give the other enantiomer,  $[\alpha]^{26D} - 25.5^\circ$ .

It was of interest to compare the relative configurations of these compounds with their silicon analogs. Using the Fregda method of quasi-racemates<sup>6,9,10</sup> it was found as expected that mixtures of (+)Ge\*H<sup>11</sup> and (+)Si\*H behave as a solid solution having at most a 1.0° melting point range over a range of concentrations, whereas mixtures of (+)Ge\*H and (–)Si\*H or (–)Ge\*H and (+)Si\*H gave melting point ranges from 10 to 25°, as shown in Fig. 2. Since the absolute configuration of (+)Si\*H has been shown to be *R*,<sup>12</sup> it follows that the absolute configuration of (+)Ge\*H is also *R* (I).



It is perhaps worthy of note that the (+) rotatory germane was obtained from the less levorotatory ether, whereas in the silicon case the (+) silane was obtained from the *more* levorotatory menthoxy ether.<sup>13</sup> Since the relative polarizabilities of groups should remain

(1) R. Schwarz and M. Lewinsohn, *Ber.*, **64**, 2352 (1931).

(1a) NOTE ADDED IN PROOF.—Since the submission of this communication the resolution of ethyl- $\alpha$ -naphthylphenylgermane has been reported: R. W. Bott, C. Eaborn and I. D. Varna, *Chem. Ind. (London)*, 614 (1963).

(2) A. G. Brook and W. W. Limburg, *J. Am. Chem. Soc.*, **85**, 832 (1963).

(3) A. G. Brook and C. M. Warner, *Tetrahedron Letters*, **18**, 815 (1962).

(4) L. H. Sommer, P. G. Rodewald and G. A. Parker, *ibid.*, **18**, 821 (1962).

(5) C. Eaborn and O. W. Steward, *Proc. Chem. Soc.*, 59 (1963).

(6) L. H. Sommer, *Angew. Chem. Intern. Ed. Engl.*, **1**, 143 (1962).

(7) O. H. Johnson and D. M. Harris, *J. Am. Chem. Soc.*, **72**, 5566 (1950).

(8) A. G. Brook, *ibid.*, **77**, 4827 (1955).

(9) A. Fregda, *Tetrahedron*, **8**, 126 (1960).

(10) K. Mislow and M. Heffer, *J. Am. Chem. Soc.*, **74**, 3668 (1952).

(11) Attached to each atom bearing an asterisk are the groups methyl,  $\alpha$ -naphthyl, and phenyl.

(12) R. S. Cahn, C. K. Ingold and V. Prelog, *Experientia*, **12**, 8 (1956).

(13) C. M. Frye, Ph.D. thesis, Pennsylvania State University, 1960.

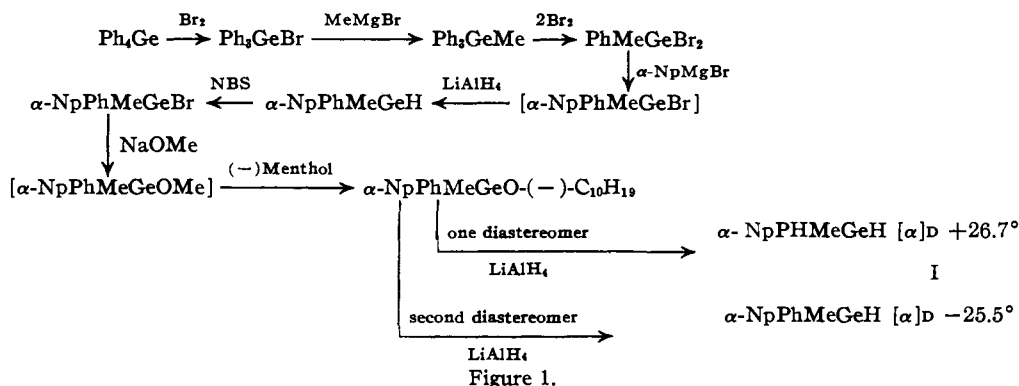


Figure 1.

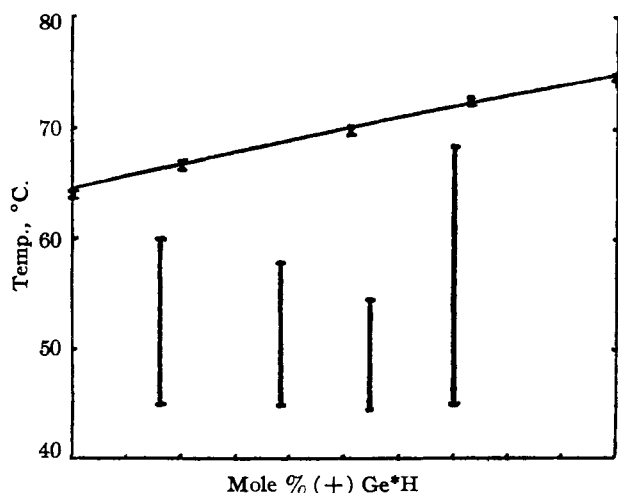


Fig. 2.—Mixture melting point diagram: upper line, (+)Ge\*H with (+)Si\*H; lower ranges, (+)Ge\*H with (-)Si\*H.

the same, regardless of whether the central atom is silicon or germanium, these results seem surprising and are being investigated.

An investigation of the stereochemistry of reactions of methyl- $\alpha$ -naphthylphenylgermane is now being undertaken in order to compare the results with those of its silicon analog. Preliminary evidence indicates that bromination of the germane involves complete racemization under a variety of conditions, whereas the silicon analog is found to brominate stereospecifically with retention of configuration<sup>13</sup> under the same conditions.

Treatment of triphenylbromogermane<sup>7</sup> in refluxing xylene with methylmagnesium iodide gave an almost quantitative yield of methyltriphenylgermane, m.p. 66–67°. Bromination with 2 mole equivalents of bromine in ethylene dibromide at 95° for 17 hr. gave 89% of methylphenyldibromogermane, b.p. 139–140° (15 mm.),  $n_D^{25}$  1.5962, which was treated with one equivalent of  $\alpha$ -naphthylmagnesium bromide in ether-benzene. On consumption of the Grignard reagent (negative Gilman color test) the entire reaction contents were added to excess lithium aluminum hydride in ether. Work-up gave 70% of methyl- $\alpha$ -naphthylphenylgermane, b.p. 155° (0.5 mm.), m.p. 50–51°. Bromination with one equivalent of N-bromosuccinimide in refluxing carbon tetrachloride gave 82% of methyl- $\alpha$ -naphthylphenylbromogermane, m.p. 58–60°.

Treatment of methyl- $\alpha$ -naphthylphenylbromogermane with slightly more than one equivalent of sodium methoxide in excess methanol, followed by replacement of the methanol with xylene by distillation, and then addition of 1.4 equivalents of (-)menthol, followed by azeotropic distillation of methanol over 12 hr., gave on distillation 90% of sirupy methyl- $\alpha$ -naphthylphenyl(-)menthoxygermane, b.p. 195–196° (0.2 mm.). This material was dissolved in two volumes of pentane

and cooled in an ice bath to give, as a first crop, 34% of methyl- $\alpha$ -naphthylphenyl(-)menthoxygermane, m.p. 86–91°,  $[\alpha]_D^{22}$  -49.3° (c 10.1, cyclohexane). Reduction of this material with lithium aluminum hydride in ether over 6 hr. gave in two crops 96% of (+)-methyl- $\alpha$ -naphthylphenylgermane, which after recrystallization from ethanol had m.p. 74–75°,  $[\alpha]_D^{25}$  +26.7° (c 10.6, cyclohexane).

Anal. Calcd. for  $\text{C}_{17}\text{H}_{16}\text{Ge}$ : C, 69.71; H, 5.51. Found: C, 69.23; H, 5.56.

After removal of additional crops of solid menthoxy compound totalling 59%, the residual oil,  $[\alpha]_D^{20}$  -59.6° (c 8.8, cyclohexane), was similarly reduced with lithium aluminum hydride to give 85% of (-)-methyl- $\alpha$ -naphthylphenylgermane, m.p. 74–75°,  $[\alpha]_D^{25}$  -25.5° (c 11.3, cyclohexane).

Bromination of (+)-methyl- $\alpha$ -naphthylphenylgermane, using either N-bromosuccinimide in carbon tetrachloride at 0° or bromine in carbon tetrachloride at 0°, gave methyl- $\alpha$ -naphthylphenylbromogermane with no observable optical activity.

Weighed samples of the appropriate silanes and germanes were dissolved in ether, and the ether then was removed under reduced pressure. The melting points of the resulting solids were then determined (Fig. 2). Analyses and infrared spectra were in agreement with the assigned structures of all compounds.

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(14) Cities Service Corporation Fellow, 1962–1963.

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### Optical Rotatory Dispersion Studies. LXXXIV.<sup>1</sup> Studies of Conformational Mobility by Low-Temperature Circular Dichroism Measurements<sup>2</sup>

Sir:

In a recent paper<sup>3</sup> we pointed out the frequent interchangeable use of the phenomenologically closely related physical methods, optical rotatory dispersion (O.R.D.) and circular dichroism (C.D.), in various stereochemical problems. Furthermore, it was emphasized<sup>3,4</sup> that, in certain instances, either O.R.D. or

(1) Paper LXXXIII: C. Djerassi, H. Wolf, D. A. Lightner, E. Bunnenberg, K. Takeda, T. Komeno and K. Kuriyama, *Tetrahedron*, in press.

(2) Supported by the National Science Foundation (Grant No. G-19905).

(3) C. Djerassi, H. Wolf and E. Bunnenberg, *J. Am. Chem. Soc.*, **84**, 4552 (1962).

(4) (a) C. Djerassi, H. Wolf and E. Bunnenberg, *ibid.*, **85**, 324 (1963); (b) K. Mislow, E. Bunnenberg, R. Records, K. Wellman and C. Djerassi, *ibid.*, **85**, 1342 (1963).