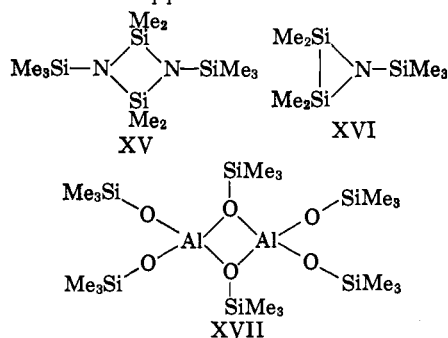


strong  $\pi$ -bonding in these molecules having planar hybridization at the nitrogen atoms.<sup>16,17</sup>

From an examination of some closely related hexamethylheterosiloxanes (IX–XI)<sup>18</sup> and nonamethylheterodisilazanes (XIII, XIV),<sup>19</sup> we could gain further knowledge of the influence of hetero-atoms on the nature of the Si–O– and Si–N– bonds. As shown in the table, we have found, that on substitution of Si by Ge, Sn, or Pb the remaining Me<sub>3</sub>Si– group(s) tend to show a steadily increasing chemical shielding and decreasing coupling constants, thus indicating increasing back-donation in the Si–O or Si–N bonds and increasing p-character of the Si valences. When compared with the corresponding data of Me<sub>3</sub>GeOGeMe<sub>3</sub><sup>20</sup> and Me<sub>3</sub>SnO–SnMe<sub>3</sub>,<sup>21</sup> the  $\delta$  and  $J$  values of the trimethylmetaloxo groups indicate the expected rehybridization of the hetero-atoms in the opposite direction.



Finally, it is interesting to note that the bridging and terminal trimethylsiloxy groups in compound XVII<sup>22</sup> show significant differences in  $J(\text{H}-^{13}\text{C})$  and  $J(\text{H}-\text{C}-^{29}\text{Si})$  and thus confirm earlier suggestions for this and some analogous "bridged" heterosiloxanes.<sup>23</sup>

**Acknowledgment.**—The author is indebted to Prof. Dr. Max Schmidt for great support.

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### The Mechanism of the Meerwein–Ponndorf–Verley Reaction

Sir:

The current view of the Meerwein–Ponndorf–Verley (MPV) reaction, recently summarized by Bradley,<sup>1</sup> is that it proceeds *via* the following steps: (1) coordination of the ketone to the alkoxide monomer; (2) hydride transfer; (3) separation from the complex of the ketone produced in step 2; (4) alcoholysis of the mixed alkoxide, liberating the free alcohol.

Step 2 is generally assumed to be rate-determining.<sup>2</sup>

Examination of the proton resonance spectra of solutions of acetone and both trimeric and tetrameric forms<sup>3</sup> of aluminum isopropoxide in toluene indicates rapid and reversible coordination of the ketone with the

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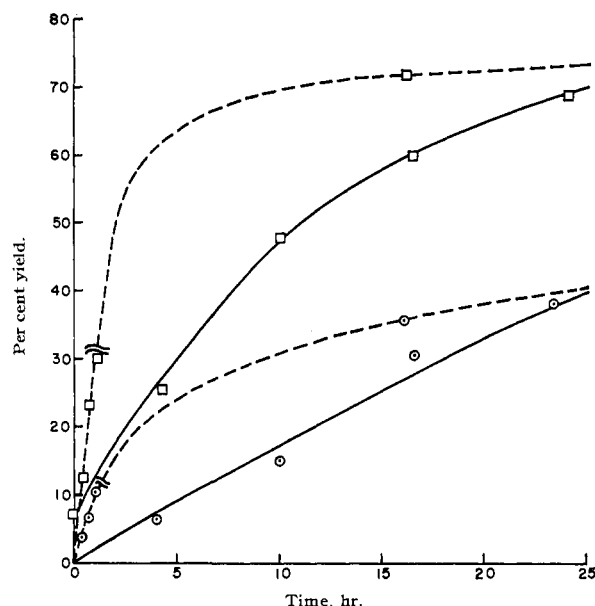


Fig. 1.—Yield of products in MPV reactions of Tables I and II:  $\square$ , acetone;  $\circ$ ,  $\alpha$ -phenylethanol; solid line, products of reaction with tetramer; dotted line, products of reaction with trimer of aluminum isopropoxide.

alkoxide. The spectra show only a single sharp acetone resonance, even at  $-35^\circ$ , its position depending on the temperature and on the ratio of alkoxide to acetone concentration. Acetone does not cause any significant change in the fairly complex proton resonance absorption pattern of the tetramer, indicating that coordination of the ketone does not involve a breakdown of the tetrameric structure. The spectrum of the trimer, however, is modified by the addition of acetone, but this may result from coordination of the ketone interfering with the rapid intramolecular alkoxide exchange taking place in this structure.

Using proton resonance spectroscopy, we have measured the rate of formation of acetone and  $\alpha$ -phenylethanol from a mixture of aluminum isopropoxide and acetophenone in 50 mole % benzene and isopropyl alcohol solvent. *Aluminum isopropoxide tetramer*, Table I, gives a considerably slower reaction than does the trimer, Table II. The results are compared in Fig. 1.

TABLE I  
REDUCTION OF ACETOPHENONE WITH ALUMINUM ISOPROPOXIDE TETRAMER<sup>a</sup>

Time, hr.	Ketone composition, mole %		$\alpha$ -Phenylethanol yield as % of theoretical yield	Molar ratio, $\alpha$ -phenylethanol/acetone
	Acetophenone	Acetone		
0	93.3	6.7	0	..
4	74.5	25.5	6.4	0.25
10	51.8	48.2	14.8	.31
16.5	40.1	59.9	30.8	.51
24	30.7	69.3	38.4	.55
48	24.4	75.6	39.2	.52
144	23.3	76.7	46.8	.61
192	22.7	77.3	51.7	.67

<sup>a</sup> Temperature  $25^\circ$ ; initial concentrations in 50 mole % benzene and isopropyl alcohol were acetophenone 0.305 M; aluminum isopropoxide 0.424 M (calculated as monomer).

In addition, it is clear that in both reactions, the rate of  $\alpha$ -phenylethanol formation is considerably lower than the rate of acetone formation, and therefore that the rate-determining step in these processes is alcoholysis of the mixed alkoxide and not hydride transfer.

TABLE II  
REDUCTION OF ACETOPHENONE WITH ALUMINUM ISOPROPOXIDE TRIMER<sup>a</sup>

Time	Ketone composition, mole %		$\alpha$ -Phenyl-ethanol yield as % of theoretical	Molar ratio, $\alpha$ -phenylethanol/acetone
	Acetophenone	Acetone		
0	100	0	0	..
10 min.	91.9	8.1	1.4	0.17
20 min.	87.1	12.9	3.7	.29
40 min.	76.7	23.3	6.6	.28
60 min.	69.6	30.4	10.4	.34
16 hr.	28.1	71.9	35.9	.50
40 hr.	26.2	73.8	42.6	.58
64 hr.	24.3	75.7	46.7	.62

<sup>a</sup> Temperature 31.4° for first hour (in n.m.r. probe) and then 25°; initial concentrations in 50 mole % benzene and isopropyl alcohol were acetophenone, 0.893 *M*; aluminum isopropoxide, 0.653 *M* (calculated as monomer).

If it is assumed that the trimer and tetramer react by the same type of mechanism, these results then show that the ketone coordinates not with aluminum alkoxide monomer formed by dissociation but directly with the trimer or tetramer by expansion of the coordination number of aluminum. The reduction could not be due to a small amount of monomer in rapid equilibrium with both trimer and tetramer because the MPV reaction is much faster than the trimer-tetramer interconversion under similar conditions. Further, the reactivity cannot be due to catalysis by a small fraction of monomer not in equilibrium with the polymeric forms because a fairly large fraction of aluminum  $\alpha$ -phenylethoxide is formed (probably as a mixed alkoxide).

The different reactivities of the slowly interconverted polymeric forms of aluminum alkoxides, and the slow alkoxide exchange with alcohols probably constitute serious sources of error in the interpretation of previously published kinetic studies of the MPV reaction.<sup>2,4</sup>

MPV reductions can thus be achieved much more rapidly and under much milder conditions than those generally employed by using aluminum isopropoxide trimer as a reagent rather than as a catalyst. This technique is aided by the miscibility of this material with most organic solvents. The reaction can be forced to completion by removal of the acetone at reduced pressure and the product recovered by hydrolysis of the aluminum alkoxide.

**Acknowledgment.**—This work has been supported in part by Grant GM 08502-02 from the National Institutes of Health.

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### Displacements at Asymmetric Germanium. Methyl- $\alpha$ -naphthylphenylgermyllithium and its Derivatives

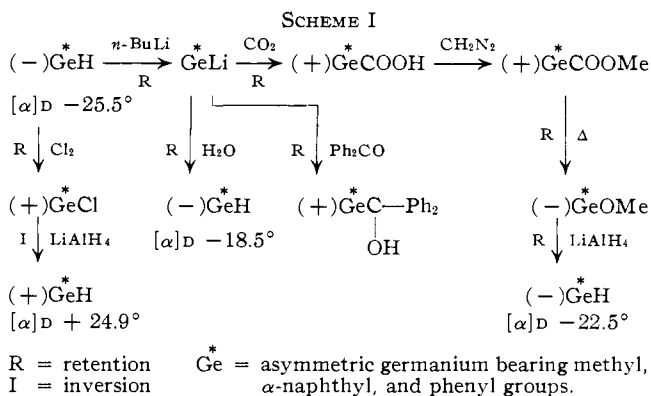
Sir:

The resolution of asymmetric organogermanium compounds has recently been achieved.<sup>1,2</sup> We now wish to report on the chemistry and stereochemistry of some displacements at germanium which occur with considerable specificity. Methyl- $\alpha$ -naphthylphenylgermyllithium has been prepared and shown to be

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highly optically stable through a sequence of reactions summarized in Scheme I.



Metalation of (-)methyl- $\alpha$ -naphthylphenylgermane, (-)GeH<sup>3</sup> with one equivalent of *n*-butyllithium in ether at room temperature over 30 min. gave a dark brown solution of GeLi, which on treatment with water gave (-)GeH containing 86% of the (-) enantiomer. Treatment of GeLi with benzophenone gave in 68% yield (+)GeCOHPh<sub>2</sub>, [ $\alpha$ ]<sup>20</sup><sub>D</sub> 6.3°, m.p. 132–134°, and carbonation of GeLi gave (+)GeCOOH, free of (-)GeH, [ $\alpha$ ]<sup>22</sup><sub>D</sub> 5.15°, m.p. 96.5–98°, dec. 110° in 66% yield. Esterification of the acid with diazomethane gave an oil, (+)GeCOOMe, [ $\alpha$ ]<sup>26</sup><sub>D</sub> 3.06°, which on thermal rearrangement from 230–270° gave 95% of (-)GeOMe, [ $\alpha$ ]<sup>26</sup><sub>D</sub> -9.75°, m.p. 54–59°, and carbon monoxide. Reduction of the methoxygermane with lithium aluminum hydride gave (-)GeH in 97% yield, [ $\alpha$ ]<sup>22</sup><sub>D</sub> -22.5°, m.p. 72–73.5° containing 94% of the original (-) enantiomer. Thus each of the four consecutive displacements at germanium occurred with essentially complete stereospecificity. Similarly (-)GeH on chlorination gave 100% of (+)GeCl, [ $\alpha$ ]<sup>28</sup><sub>D</sub> +6.32°, m.p. 68–69° which on reduction gave (+)GeH, [ $\alpha$ ]<sup>27</sup><sub>D</sub> +24.9°, in 99% yield, another Walden cycle with high over-all stereospecificity.<sup>1</sup>

All of the reactions except the reduction of GeCl are believed to take place with retention of configuration at germanium. If so, then (-)GeH, (+)GeCOOH, (-)GeOMe, (+)GeCOHPh<sub>2</sub>, and (+)GeCl will all have the same absolute configuration with respect to the methyl,  $\alpha$ -naphthyl, and phenyl groups. It is known from previous studies that (-)SiH, (-)SiOMe,<sup>4</sup> (+)SiCOHPh<sub>2</sub>,<sup>5</sup> and (+)SiCl<sup>4</sup> have the same configuration and that (-)GeH<sup>2</sup> and (-)SiH have the same configuration. It has now been shown by mixed melting points between pairs of enantiomers<sup>2</sup> that (-)GeOMe and (-)SiOMe have the same configurations, as do (+)GeCOHPh<sub>2</sub> and (+)SiCOHPh<sub>2</sub>, and (+)GeCl and (+)SiCl. Hence

(3) Compounds described as GeH, SiCl, GeOMe, etc., each have methyl,  $\alpha$ -naphthyl, and phenyl groups attached to the metalloid atom and are optically active.

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