

TABLE II
REDUCTION OF ACETOPHENONE WITH ALUMINUM ISOPROPOXIDE TRIMER^a

Time	Ketone composition, mole %		α -Phenyl-ethanol yield as % of theoretical	Molar ratio, α -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

^a 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 α -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.^{2,4}

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.

(4) L. M. Jackman and A. K. Macbeth, *J. Chem. Soc.*, 3252 (1952); M. S. Bains and D. C. Bradley, *Chem. Ind.* (London), 1032 (1961).

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Displacements at Asymmetric Germanium. Methyl- α -naphthylphenylgermyllithium and its Derivatives

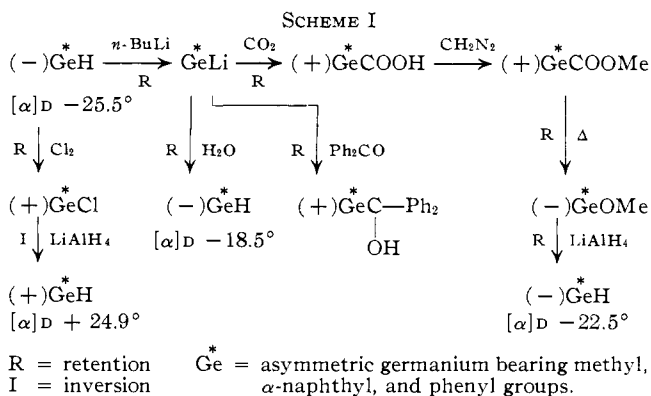
Sir:

The resolution of asymmetric organogermanium compounds has recently been achieved.^{1,2} We now wish to report on the chemistry and stereochemistry of some displacements at germanium which occur with considerable specificity. Methyl- α -naphthylphenylgermyllithium has been prepared and shown to be

(1) R. W. Bott, C. Eaborn and I. D. Varna, *Chem. Ind.* (London), 614 (1963).

(2) A. G. Brook and G. J. D. Peddle, *J. Am. Chem. Soc.*, **85**, 1869 (1963)

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



Metalation of (-)methyl- α -naphthylphenylgermane, (-)GeH³ 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 (+)GeCOHPh₂, [α]²⁰_D 6.3°, m.p. 132–134°, and carbonation of GeLi gave (+)GeCOOH, free of (-)GeH, [α]²²_D 5.15°, m.p. 96.5–98°, dec. 110° in 66% yield. Esterification of the acid with diazomethane gave an oil, (+)GeCOOMe, [α]²⁶_D 3.06°, which on thermal rearrangement from 230–270° gave 95% of (-)GeOMe, [α]²⁶_D -9.75°, m.p. 54–59°, and carbon monoxide. Reduction of the methoxygermane with lithium aluminum hydride gave (-)GeH in 97% yield, [α]²²_D -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, [α]²⁸_D +6.32°, m.p. 68–69° which on reduction gave (+)GeH, [α]²⁷_D +24.9°, in 99% yield, another Walden cycle with high over-all stereospecificity.¹

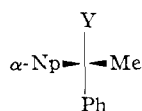
All of the reactions except the reduction of GeCl are believed to take place with retention of configuration at germanium. If so, then (-)GeH, (+)GeCOOH, (-)GeOMe, (+)GeCOHPh₂, and (+)GeCl will all have the same absolute configuration with respect to the methyl, α -naphthyl, and phenyl groups. It is known from previous studies that (-)SiH, (-)SiOMe,⁴ (+)SiCOHPh₂,⁵ and (+)SiCl⁴ have the same configuration and that (-)GeH² and (-)SiH have the same configuration. It has now been shown by mixed melting points between pairs of enantiomers² that (-)GeOMe and (-)SiOMe have the same configurations, as do (+)GeCOHPh₂ and (+)SiCOHPh₂, and (+)GeCl and (+)SiCl. Hence

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

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

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

there is complete correspondence with respect to configuration between germanium and silicon enantiomers with the same sign of rotation. In addition, Brewster's rules of atomic asymmetry, which in the case of methyl α -naphthylphenylsilyl compounds correctly predict the configurations of the H, Cl, Br, OH, OMe, and other derivatives,⁶ predict the same configuration, *viz.*



for $(-)\text{GeH}$, $(+)\text{GeCOOH}$, $(-)\text{GeOMe}$, $(+)\text{GeCl}$, and their silicon analogs. Hence, it follows that retention of configuration is involved in each of the reactions so specified in Scheme I, and that in all similar cases studied to date (except bromination²), the stereochemistry of displacements at asymmetric germanium is the same as that of displacements at silicon.

The stereochemistry described above is in accord with other known reactions. Studies on vinyl metallics,⁷ and other organometallic systems⁸ indicate that metalation, or halogen-metal exchange, carbonation, and addition to a carbonyl group each occur with retention of configuration. Thermal rearrangements of silane- and germanocarboxylates to ethers have been shown to be intramolecular processes,⁹ and would be expected to involve "flank" attack, leading to retention of configuration. Similar results were found in the intramolecular rearrangements of α -hydroxysilanes to silyl ethers.^{5,6}

The most significant result of this study is the remarkable optical stability of methyl- α -naphthylphenylgermyllithium, which through the carbonation cycle, is shown to have essentially complete optical stability in ether at room temperature over 30 min. While organometallics such as *sec*-butyllithium¹⁰ have considerable optical stabilities in hexane at low temperatures, the presence of diethyl ether leads to rapid racemization. Further studies are in progress.

Configurational relationships were established by weighing known quantities of silicon and germanium enantiomers, dissolving them in ether or pentane and immediately pumping off the solvent. Compounds of like configuration had narrow mixed melting point ranges, whereas compounds of unlike configuration had melting point ranges of from 10 to 25°. Analyses and infrared spectra were in accord with the assigned structures of all compounds.

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

(7) D. Y. Curtin and J. W. Crump, *ibid.*, **80**, 1922 (1958).

(8) H. M. Walborsky and F. J. Impastato, *ibid.*, **81**, 5835 (1959); H. M. Walborsky and A. E. Young, *ibid.*, **83**, 2595 (1961).

(9) A. G. Brook, *ibid.*, **77**, 4827 (1955); A. G. Brook and R. J. Mauris, *ibid.*, **79**, 971 (1957).

(10) D. Y. Curtin and W. J. Koehl, *ibid.*, **84**, 1967 (1962).

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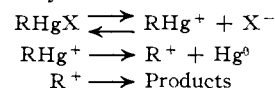
Generation of Phenyl Radical *via* Reduction of Phenylmercuric Cation

Sir:

The solvolysis of alkylmercuric salts such as acetate (or more effectively perchlorate) has been well established to be a general route to afford carbonium ions.¹ Among the many possible mechanisms proposed for this

(1) F. R. Jensen and R. J. Ouellette, *J. Am. Chem. Soc.*, **83**, 4477, 4478 (1961); **85**, 363 (1963).

reaction,²⁻⁴ the most probable and simplest one as outlined by Jensen and Ouellette¹ involves the ionization of alkylmercuric salt followed by dissociation of carbon mercury linkage to yield carbonium ion and mercury.



Robson and Wright⁴ pointed out that phenylmercuric acetate does not undergo heterolysis in methanol with boron trifluoride. Jensen and Ouellette in their elegant work also emphasized that the reaction has been found to be general for all alkyl groups, and the ionic mechanism is beyond doubt; however, the fate of solvolysis of phenylmercuric salts was not mentioned.

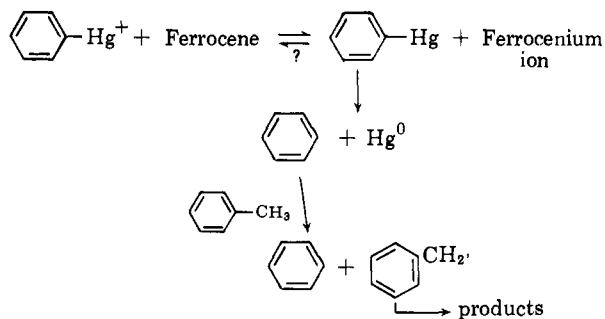
In our Laboratories we have found that phenylmercuric acetate, preferably perchlorate or tosylate, undergoes solvolysis in acetic acid or even toluene in the presence of a reducing agent. For example, with ferrocene, the reaction furnishes the phenyl radical with concomitant oxidation of ferrocene to ferrocenium ion.

Phenylmercuric acetate (Eastman Kodak White Label, m.p. 148-150°) in acetic acid reacts with ferrocene very slowly, as indicated by the gradual appearance of the characteristic blue color of ferrocenium ion. Addition of a catalytic amount of perchloric acid to the mixture led to almost instantaneous formation of the characteristic ferrocenium ion color. Using acrylonitrile as solvent, phenylmercuric acetate and ferrocene initiated polymerization of the monomer and the polymerization process was inhibited by both free radical scavengers such as *p*-hydroquinone and ions such as NaCl, NaNO₂, etc. When the reaction was carried out in toluene with an equimolar (0.1 mmole) amount of phenylmercuric acetate, perchloric acid, and ferrocene, the appearance of ferrocenium ion color was instantaneous and the yield of benzene was practically quantitative. With toluenesulfonic acid, the yield of benzene was 25%.

The previous failure to observe the cleavage of phenyl-mercury bond⁴ is perhaps indicative of the unfavorable energetics for such heterolysis and may be attributed at least partially to the stabilization of phenylmercuric cation by dissipating the positive charge to the aromatic ring.



Since the solvolytic step is reversible, no appreciable demercuration of this cation is anticipated. In the presence of a reducing agent such as ferrocene, the intermediate cation from solvolysis is reduced to phenylmercury (I), followed by demercuration and formation of phenyl radical. When the reaction is carried out in toluene, the phenyl radical abstracts hydrogen from toluene to form benzene and the more stable benzyl radical.⁵



(2) K. Ichikawa and H. Ouchi, *ibid.*, **82**, 3876 (1960).

(3) S. Winstein, *et al.*, *ibid.*, **77**, 3741 (1955); *Chem. Ind. (London)*, 251 (1962).

(4) J. H. Robson and G. F. Wright, *Can. J. Chem.*, **38**, 21 (1960).

(5) S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, **77**, 3628 (1955).