of PPA was stirred at 75° for 1.5 hr. and treated as above. Distillation yielded 12.1 g. of phenyl acetate and 46.5 g. (51%) of 4-acetylphenyl acetate, b.p. 165–170° (19 mm.), m.p. 48–51°. Crystallization from ethyl acetate–petroleum ether (50–60°) raised the m.p. to 52–54°. A mixture with authentic material had the same m.p.

(b) **From Phenyl Acetate.**—A solution of 45.0 g. of phenyl acetate, 30.0 g. of acetic acid and 250 g. of PPA was stirred at 75° for 1.5 hr. and treated as above to give 9.02 g. of recovered starting material and 30.1 g. (50%) of 4-acetylphenyl acetate, m.p. 51–53°.

Rearrangement of Phenyl Benzoate.—A mixture of 30.0 g. of phenyl benzoate and 220 g. of PPA was stirred at 80° for 2.5 hr. Hydrolysis with ice and water followed by extraction with a benzene–ether solution afforded a heterogeneous organic mixture. Extraction of this with 10% sodium hydroxide solution followed by acidification of the aqueous phase gave 7.5 g. (25%) of 4-hydroxybenzophenone, m.p. 132–134°. When a sample of this was mixed with authentic material the m.p. was unchanged. The organic phase from the extraction was evaporated to dryness under reduced pressure and the residue crystallized twice from methanol–water to give 4.0 g. (13%) of 4-benzoylphenyl benzoate, m.p. and mixture m.p. 111–113°.

Rearrangement of Resorcyl Diacetate.—A mixture of 100 g. of resorcyl diacetate and 400 g. of PPA was stirred at 70° for 2 hr. and worked up as in the previous examples. There was obtained 19.1 g. (19.1%) of 4,6-diacetylresorcinol, m.p 179–180°. One crystallization from ethyl acetate–cyclohexane raised the m.p. to 181–182° (lit.[7] 182°).

Attempted Rearrangement of 2-Hydroxyacetophenone.—Forty grams of freshly distilled 2-hydroxyacetophenone[8] (b.p. 110–112° at 19 mm.) was heated with 200 g. of PPA for 15 min. at 95°. Isolation in the usual manner afforded 28.1 g. of starting material, b.p. 110° (19 mm.). No forerun or pot residue was obtained. A similar experiment in which the time was extended to 1.5 hr. gave no distillable product.

Acetylation of Phenyl Benzoate.—A mixture of 30.0 g. of phenyl benzoate, 10.5 g. of acetic acid and 220 g. of PPA was stirred at 90° for 1 hr. The usual isolation technique gave 7.7 g. (21%) of 4-acetylphenyl benzoate, m.p. 132–134°. Crystallization from methanol–water raised the m.p. to 135–136°, not depressed on admixture with an authentic sample. Except for starting material no other product could be isolated.

Benzoylation of Phenyl Acetate.—A mixture consisting of 20.0 g. of phenyl acetate, 20.7 g. of benzoic acid and 220 g. of PPA was stirred at 85–90° for 1 hr. and submitted to the normal isolation technique. There was obtained, after one crystallization of the crude product from ethyl acetate–petroleum ether (50–60°), 7.5 g. (21%) of 4-acetylphenyl benzoate, m.p. 134–135°. A mixture m.p. with authentic material was not depressed. Chromatography of the mother liquor (after dilution with petroleum ether) on acid-washed alumina gave an additional 0.4 g. of the above benzoate melting at the same temperature and 1.1 g. (3%) of 4-benzoylphenyl acetate, m.p. and mixed m.p. 79–80°.

(7) K. W. Rosenmund and W. Schnurr, *Ann.*, **460**, 56 (1928).
(8) E. Klarmann, THIS JOURNAL, **48**, 2358 (1926).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF TEXAS
AUSTIN, TEXAS

The Formation of Hexaphenyldigermane and Carbon Monoxide from the Reaction of Triphenylgermyllithium with Some Esters

BY HENRY GILMAN AND CLARE W. GEROW

In the course of investigations in this Laboratory an attempt was made to prepare alcohols and ketones containing the triphenylgermyl grouping attached to the carbinol or carbonyl carbon atom. Thus the reaction of triphenylgermyllithium with methyl triphenylgermanecarboxylate was investigated relative to the possibility of preparing bis-(triphenylgermyl) ketone or tris-(triphenylgermyl)-carbinol. However, instead of obtaining these products, carbon monoxide was vigorously evolved and hexaphenyldigermane was the only other product isolated.
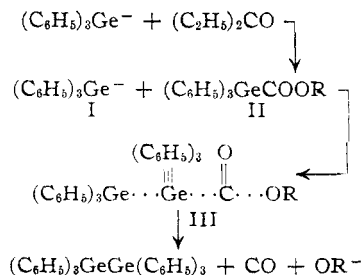
$$(C_6H_5)_3GeLi + (C_6H_5)_3GeCOOCH_3 =$$
$$(C_6H_5)_3GeGe(C_6H_5)_3 + CO + LiOCH_3$$
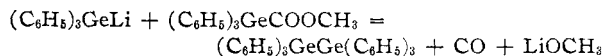
Since the triphenylgermyllithium had been prepared from the cleavage of tetraphenylgermane,[1] the hexaphenyldigermane must have been a product of the reaction rather than unreacted starting material. Also, hexaphenyldigermane has never been isolated from the hydrolysis of triphenylgermyllithium, thus eliminating this reaction as a possible source of the hexaphenyldigermane.

An attempt to prepare the bis-(triphenylgermyl) ketone by the reaction of triphenylgermyllithium with diethyl carbonate again resulted in the evolution of carbon monoxide and the isolation of hexaphenyldigermane as the sole product.

Due to the symmetry of hexaphenyldigermane it was unclear where each germanium atom originated in the reaction of methyl triphenylgermanecarboxylate with triphenylgermyllithium. Accordingly the reaction of triphenylsilyllithium with methyl triphenylgermanecarboxylate was examined. In this reaction carbon monoxide was again vigorously evolved and the only other product isolated was triphenylsilyltriphenylgermane, thus indicating that in the analogous reaction of triphenylgermyllithium with methyl triphenylgermanecarboxylate, one atom of germanium in hexaphenyldigermane came from the ester and one atom from the triphenylgermyllithium reagent.

The nature of this reaction indicates that it may be of value in synthesizing other compounds of germanium containing silicon, tin or lead bound directly to the germanium atom. Studies with this view in mind are now in progress as well as reactions concerned with the mechanism of this decarbonylation.[2]

A possible mechanism would be the attack of the triphenylgermyl cation (I) on the germanium atom of the triphenylgermanecarboxylic acid ester (II) with the formation of a pentacovalent intermediate (III). In the case of the reaction of triphenylgermyllithium with diethyl carbonate, it is assumed that ethyl triphenylgermanecarboxylate is the initial product formed.

$$(C_6H_5)_3Ge^- + (C_2H_5)_2CO$$

$$(C_6H_5)_3Ge^- + (C_6H_5)_3GeCOOR$$
$$\quad\quad I \quad\quad\quad\quad\quad II$$

$$\overset{(C_6H_5)_3}{\underset{}{}}\ \overset{O}{\underset{}{}}$$
$$(C_6H_5)_3Ge\cdots Ge\cdots C\cdots OR$$
$$\quad\quad\quad III$$

$$(C_6H_5)_3GeGe(C_6H_5)_3 + CO + OR^-$$

(1) It has been found in this Laboratory that triphenylgermyllithium may be prepared from the cleavage of hexaphenyldigermane, tetraphenylgermane or triphenylchlorogermane by lithium in ethylene glycol dimethyl ether.
(2) The mechanism of similar base-catalyzed eliminations of carbon monoxide from triphenylsilanecarboxylic acid and its esters is discussed by A. G. Brook and H. Gilman, THIS JOURNAL, in press.

Experimental[3]

Preparation of Triphenylgermyllithium.—To a nitrogen-flushed flask was added 7.12 g. (0.0187 mole)[4] of tetraphenylgermane, 2.0 g. (0.288 g. atom)[5] of lithium wire, cut into 2–3 mm. lengths, and about 5 ml. of sodium-dried, redistilled ethylene glycol dimethyl ether. After about 40 minutes the reaction had started as was evidenced by the development of a brown color.[6] After the color deepened to a very dark brown (usually 1–2 hours after reaction began) an additional 20 ml. of solvent was added and the mixture was stirred until there was no evidence of unreacted solid (usually 4–5 hours after the reaction has begun).[7] The dark-colored solution was pipetted into a dropping funnel and the residual lithium washed with solvent, with the washings being added to the main solution.

Yields of products from many reactions of triphenylgermyllithium indicate that the reagent is obtained in approximately 70% yield. In no reaction has there been isolated any product from the phenyllithium which should be present from the cleavage of tetraphenylgermane with lithium. Presumably it is destroyed by reaction with the solvent.

Reactions of Triphenylgermyllithium. With Methyl Triphenylgermanecarboxylate.—A triphenylgermyllithium solution as prepared above from 7.12 g. of tetraphenylgermane was added portionwise to 1.82 g. (0.005 mole) of methyl triphenylgermanecarboxylate[8] dissolved in 20 ml. of ethylene glycol dimethyl ether. Immediately upon this addition, a gas was evolved vigorously which blackened a piece of filter paper moistened with a dilute solution of palladium chloride[9]; thus indicating that the gas was carbon monoxide. In addition, heat was generated and a white solid precipitated. When the addition was complete the mixture was stirred 18 hours then hydrolyzed by pouring it into a mixture of ammonium chloride and crushed ice. When the ice melted the mixture was filtered and the precipitate was washed with ether. The remaining solid weighed 2.5 g. and melted over the range 328–340°. Recrystallization from benzene gave 2.3 g. (75% yield based on methyl triphenylgermanecarboxylate) of hexaphenyldigermane (mixed melting point) melting 340–342°. The aqueous solution was extracted three times with ether and the combined ether washings were dried over anhydrous sodium sulfate. The solvent was removed by distillation leaving a small amount of oil from which no products have been isolated.

With a Deficiency of Diethyl Carbonate.—A solution of triphenylgermyllithium as prepared above was added portionwise to a stirring solution of 0.59 g. (0.005 mole) of freshly distilled diethyl carbonate dissolved in 20 ml. of ethylene glycol dimethyl ether. Carbon monoxide was again evolved vigorously (palladium chloride test), heat was generated and a white solid precipitated. After the addition was complete the mixture was stirred 12 hours then worked up as previously to yield 2.7 g. (88% based on diethyl carbonate) of hexaphenyldigermane melting 340–342°.

With an Excess of Diethyl Carbonate.—A repeat of the previous experiment using 1.18 g. (0.01 mole) of diethyl carbonate and triphenylgermyllithium from the cleavage of 3.81 g. (0.01 mole) of tetraphenylgermane gave 1.4 g. (47%

based on tetraphenylgermane) of hexaphenyldigermane melting 338–340°. Working up the ether portions gave 0.45 g. of a substance as yet unidentified melting 98–99°.

Reaction of Triphenylsilyllithium with Methyl Triphenylgermanecarboxylate.—Triphenylsilyllithium was prepared in ethylene glycol dimethyl ether from 5.19 g. (0.01 mole) of hexaphenyldisilane in accordance with recent directions,[10] and added portionwise to 1.82 g. (0.005 mole) of methyl triphenylgermanecarboxylate dissolved in 20 ml. of ethylene glycol dimethyl ether. Carbon monoxide was evolved, heat was generated and a solid precipitated. Working up the mixture as described previously gave 2.45 g. (84% based on methyl triphenylgermanecarboxylate) of triphenylsilyltriphenylgermane melting 357–359°. A mixed melting point with an authentic sample prepared from the reaction of triphenylsilylpotassium[11] with triphenylchlorogermane showed no depression.

(10) A. G. Brook and H. Gilman, This Journal, **76**, 278 (1954).

(11) H. Gilman and T. C. Wu, J. Org. Chem., **18**, 753 (1953).

Department of Chemistry
Iowa State College
Ames, Iowa

Studies on the Reversal of the Mannich Reaction

By Kenneth A. Kun[1] and Paul E. Spoerri

Taber,[2] while studying the addition of bases to polar hydrocarbons, attempted to cause the addition of piperidine to the exocyclic double bond of 2,3,4,5-tetraphenylfulvene. Instead of the desired product, 1-(N-piperidylmethyl)-2,3,4,5 tetraphenylcyclopenta-2,4-diene,2,3,4,5-tetraphenylcyclopenta-2,4-diene was obtained. This reaction appeared to be a reversal of the formation of a Mannich base of a hydrocarbon. Taber went on to show that 2,5-diphenyl-3,4-(4'-methoxyphenyl)-fulvene reacted in the same manner. The discovery of this type of reversal of the Mannich reaction and its application to the synthesis of two tetraphenylcyclopentadienes with yields better than previously reported[3] gave hopes that this was a superior general method of synthesis for substituted tetraphenylcyclopentadienes through the usually available tetraphenylcyclones. The preparation of some *para* substituted tetraphenylfulvenes and their conversion to the corresponding dienes were studied in this work.

2,4,5-Triphenyl-3-(4'-tolyl)-fulvene (I) was prepared from 2,4,5-triphenyl-3-(4'-tolyl)-cyclopenta-2,4-diene-1-one[4,5] by the formation of the corresponding tertiary carbinol *via* the Grignard reaction using methylmagnesium iodide which in turn was dehydrated easily to the desired fulvene. Treating

(3) All melting points are uncorrected. Reactions involving organometallic compounds were carried out in an atmosphere of dry, oxygen-free nitrogen.

(4) Runs made using amounts of tetraphenylgermane in excess of 40 g. gave poor results due to the fact that the two phase reaction requires such long reaction time that side reactions involving the soluble triphenylgermyllithium, the solvent and the lithium metal reduced the concentration of the triphenylgermyllithium.

(5) A large excess of lithium is desirable due to the fact that tetraphenylgermane is insoluble in the solvent and the large metal excess permits better contact of the reactants.

(6) In a large number of preparations it has been observed that the time required for the color to appear varies from 5 minutes to 2.5 hours. The reaction starts faster if the amount of solvent added initially is kept to a minimum. Reactions which failed to start when too much solvent was added initially developed a color when the excess solvent was removed by evaporation in a stream of nitrogen.

(7) It has been observed that the concentration of triphenylgermyllithium decreases with time, presumably by reaction with the solvent, so it is necessary to use the reagent as soon as it is prepared.

(8) A. G. Brook and H. Gilman, This Journal, **76**, 77 (1954).

(9) R. Nowicki, Chem. Z., **35**, 1120 (1911).

(1) The material reported here is a portion of the thesis for the degree of Master of Science in Chemistry presented by Kenneth A. Kun to the Graduate School of the Polytechnic Institute of Brooklyn, September, 1954.

(2) D. Taber, E. I. Becker and P. E. Spoerri, This Journal, **76**, 776 (1954).

(3) L. Mehr, Dissertation, Polytechnic Institute of Brooklyn, June, 1953.

(4) D. Trucker, Dissertation, Polytechnic Institute of Brooklyn, June, 1951.

(5) W. Dilthey, O. Trösken, K. Plum and W. Schommer, J. prakt. Chem., **141**, 331 (1934).