THE JOURNAL OF Organic Chemistry®

Volume 22, Number 9

September 17, 1957

Behavior of Triphenylsilane, Triphenylgermane, and Triphenyltin Hydride in the Presence of Olefins[1a]

RICHARD FUCHS[1b] AND HENRY GILMAN

Received January 3, 1957

The addition of triphenylsilane, triphenylgermane, and triphenyltin hydride to cyclohexene and of triphenylgermane to 1,1-diphenylethylene has been studied. Triphenyltin hydride does not add to octene-1 but gives a redistribution product, tetraphenyltin. Triphenylgermane adds to octene-1 and to cyclohexene when the reaction is initiated by either benzoyl peroxide or ultraviolet irradiation, but peroxide initiation fails to cause its addition to 1,1-diphenylethylene. Triphenylsilane adds to octene-1 when peroxide initiation is used, but not under ultraviolet irradiation. Several addition products were prepared by independent syntheses.

The addition of trichlorosilane to a variety of olefins under the influence of peroxide, ultraviolet irradiation, or heat has been reported[2] in a number of publications. More recently triphenylsilane has been added to the carbon-carbon double bond of 9-undecenoic acid,[3a] ethyl 9-undecenoate[3a] and several olefins,[3b] and a variety of silicon hydrides have been added to double-bonded compounds,[3c] in peroxide-catalyzed reactions. Addition reactions have also been reported for trichlorogermane[3d] and for triphenyl- and tributyltin hydrides.[3e]

A comparison of the behavior of triphenylsilane, triphenylgermane, and triphenyltin hydride towards 1-octene with peroxide and ultraviolet initiation has now been made. Also the reactions of triphenylgermane with 1,1-diphenylethylene and with cyclohexene have been studied.

Both triphenylsilane and triphenylgermane added readily to 1-octene under the influence of peroxide.

$$(C_6H_5)_3GeH + C_6H_{13}CH{=}CH_2 \longrightarrow (C_6H_5)_3GeCH_2CH_2C_6H_{13}$$

Triphenyltin hydride afforded only the redistribution product tetraphenyltin. Triphenylgermane did not react with 1,1-diphenylethylene, but the reaction with cyclohexene produced the expected addition product along with tetraphenylgermane. Ultraviolet irradiation failed to initiate the reaction of triphenylsilane with 1-octene, but successfully initiated the addition of triphenylgermane to 1-octene, the addition of triphenylgermane to cyclohexene accompanied by redistribution, and the redistribution of triphenyltin hydride, about as effectively as did peroxide. Triphenyltin hydride was found to be stable to redistribution in the absence of light and peroxide. The use of phenylazotriphenylmethane, which furnishes radicals at a relatively low temperature, also led to the formation of tetraphenyltin from triphenyltin hydride, rather than to the product of addition.

Authentic samples of the expected addition products were prepared from triphenylchlorosilane, triphenylchlorogermane or triphenyltin chloride

---

[1a] A preliminary report of this work was presented at the 66th meeting of the Iowa Academy of Sciences held at Iowa State College, April 30 and May 1, 1954.

[1b] Department of Chemistry, University of Texas, Austin 12, Texas.

[2] L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, *J. Am. Chem. Soc.*, **69**, 188 (1947); *Ibid.*, **70**, 484 (1948); C. A. Burkhard and R. R. Krieble, *J. Am. Chem. Soc.*, **69**, 2687 (1947); A. J. Barry, L. De Pree, J. Gilkey, and D. E. Hook, *J. Am. Chem. Soc.*, **69**, 2916 (1947); R. Calas and E. Frainnet, *Bull. soc. chim. France*, 241 (1952); N. Duffant and R. Calas, *Bull. soc. chim. France*, 241 (1952); R. Calas and N. Duffant, *Bull. soc. chim. France*, 792 (1953); E. Frainnet, *Bull. soc. chim. France*, 792 (1953); R. Calas, E. Frainnet, and J. Valade, *Bull. soc. chim. France*, 793 (1953).

[3a] G. N. Gadsby, *Research (London)*, **3**, 338 (1950). (b) H. Merten and H. Gilman, *J. Am. Chem. Soc.*, **76**, 5798 (1954). (c) J. L. Speier, R. Zimmerman, and J. Webster, *J. Am. Chem. Soc.*, **78**, 2278 (1956). (d) A. K. Fischer, R. C. West, and E. G. Rochow, *J. Am. Chem. Soc.*, **76**, 5878 (1954). (e) G. J. M. Van der Kerk, J. G. A. Luijten, and J. G. Noltes, *Chemistry and Industry*, 352 (1956); G. J. M. Van der Kerk and J. G. A. Luijten, *J. Appl. Chem. London*, **6**, 49, 56, 93 (1956); H. Gilman and J. Eisch, *J. Org. Chem.*, **20**, 763 (1955).

and the appropriate alkyl Grignard or lithium reagent.

$$(C_6H_5)_3SnCl + C_8H_{17}MgBr \longrightarrow (C_6H_5)_3SnC_8H_{17}$$

The structure of each radical-addition product was confirmed by the nondepression of the melting point of an authentic sample of the compound, and by the identity of the infrared absorption spectra.

EXPERIMENTAL[4]

Addition of triphenylsilane to 1-octene with peroxide initiation. A mixture of 20.8 g. (0.08 mole) of triphenylsilane,[5] 25 ml. of petroleum ether (b.p. 60–70°), 1.1 g. (0.01 mole) of 1-octene and 0.30 g. (0.00012 mole) of benzoyl peroxide was placed in a 100-ml. flask. The system was flushed for 5 min. with a brisk stream of nitrogen, and subsequently a positive nitrogen pressure was maintained. The mixture was heated for 48 hr. in an oil bath kept at 75°. Afterwards distillation of the slightly yellow solution through a Vigreux column yielded first, solvent, second, a little biphenyl, third, a factor rich in unchanged triphenylsilane, b.p. 138–182° at 0.5 mm., and finally, triphenyl-1-octylsilane, b.p. 182° at 0.5 mm. to 192° at 0.2 mm. The latter fraction after one recrystallization from ethanol gave 2.0 g. (54%) of crystals, m.p. 64–69°. Two additional recrystallizations afforded 1.4 g. (38%) of material melting at 70.0–71.5°.

An authentic sample of triphenyl-1-octylsilane, m.p. 72.5–73.5°, prepared from triphenylchlorosilane and 1-octylmagnesium bromide, was kindly supplied by Dr. Ronald Meen of this laboratory. A mixture of the two samples melted at 71–73°. The infrared absorption spectra in carbon disulfide solution were identical.

Ultraviolet irradiation of triphenylsilane and 1-octene. A mixture of 20.8 g. (0.08 mole) of triphenylsilane, 25 ml. of *n*-heptane and 1.7 ml. (0.01 mole) of 1-octene was irradiated in a quartz flask for 48 hr. by a 125-watt ultraviolet lamp placed at about 1 cm. below the flask. The contents of the flask were kept below about 40° by a continuous stream of air impinging on the bottom of the flask. The solvent was distilled through a Vigreux column. Some unchanged 1-octene came over with the heptane, and could be detected by the odor and by the instantaneous reduction of permanganate in acetic acid solution. Distillation of the residue yielded triphenylsilane, b.p. 127–134° at 0.25 mm., but no higher boiling material suggestive of triphenyl-1-octylsilane. A brown, tarry residue of less than 0.5 g. remained in the flask.

Preparation of triphenyl-1-octylgermane from triphenylchlorogermane and 1-octyllithium. A solution of 1-octyllithium[6] was prepared from 17.3 ml. (0.10 mole) of 1-bromooctane and 1.53 g. (0.22 g. atom) of lithium wire in ether solution at 0°. The yield determined by the double titration procedure[7] was 67%. To 0.063 mole of the 1-octyllithium solution was added a solution of 5.1 g. (0.015 mole) of triphenylchlorogermane[8] in 100 ml. of ether at room temperature over 0.5 hr. After 1 hr. of stirring, 100 ml. of toluene was added, and solvent was distilled until the vapor temperature reached 105°. Hydrolysis was then effected by the slow addition of 150 ml. of cold water with external ice cooling of the flask. Some petroleum ether was added and the layers were separated. The organic layer was dried over magnesium sulfate. Two recrystallizations from about 50 ml. of ethanol gave 3.9 g. (62%) of triphenyl-1-octylgermane, m.p. 72–73°.

Addition of triphenylgermane to 1-octene with peroxide initiation. The procedure used was similar to that employed with triphenylsilane, 1-octene, and peroxide. In a dry flask were mixed 21.4 g. (0.07 mole) of triphenylgermane,[9] m.p. 45.5–47.0°, 25 ml. of petroleum ether (b.p. 60–70°), 1.7 ml. (0.01 mole) of 1-octene and 0.3 g. of benzoyl peroxide. The mixture was heated in a 75° bath for 24 hr. Distillation afforded unchanged triphenylgermane, b.p. 143–151° at 0.25 mm., and 3.8 g. (91%) of product, b.p. 190–198° at 0.25 mm., m.p. 57–67°. Two recrystallizations from ethanol raised the melting point to 71–72°. A mixture of the latter sample with triphenyl-1-octylgermane (m.p. 72–73°) melted at 71.5–72.0°. The identity of the two materials was confirmed by the infrared spectra.

Anal.[10] Calcd. for $C_{26}H_{32}Ge$: Ge, 17.4. Found: Ge, 17.5, 17.7.

Addition of triphenylgermane to 1-octene with ultraviolet initiation. A mixture of 0.045 mole of triphenylgermane, 0.006 mole of 1-octene and 25 ml. of heptane in a quartz flask was irradiated for 48 hr. The solid material which distilled at 170–195° at 0.15 mm. and was recrystallized from ethanol weighed 2.0 g. (80%), and melted at 69–70.5°. A mixture with authentic triphenyl-1-octylgermane (m.p. 72–73°) melted at 72–73°. A white, ethanol-insoluble residue was recovered from the recrystallization of this triphenyl-1-octylgermane. Recrystallization of the residue from a benzene ($^2/_3$)-ethanol ($^1/_3$) mixture gave 0.4 g. of solid, m.p. 232–234°. A mixture of this material with authentic tetraphenylgermane (m.p. 227.5–230.0°) melted at 228.0–232.5°.

Preparation of triphenylcyclohexylgermane from triphenylchlorogermane and cyclohexylmagnesium bromide. Cyclohexylmagnesium bromide was prepared by the dropwise addition of a solution of 24.6 ml. (0.20 mole) of bromocyclohexane in 50 ml. of ether to a mixture of 5.0 g. (0.205 g. atom) of magnesium turnings in 150 ml. of ether. The mixture was refluxed for 3 hr., was allowed to stand overnight, and was filtered through glass wool. Then a solution of 10.2 g. (0.03 mole) of triphenylchlorogermane[9] in 100 ml. of benzene was added dropwise to the black Grignard solution. The mixture was refluxed for 4 hr. and was allowed to stand overnight. Water was added dropwise with ice cooling. The organic layer was separated and dried over magnesium sulfate. Most of the benzene was distilled, and the residue was recrystallized from ethanol. The product weighed 3.6 g. (31%) and melted at 137–145°. Further recrystallization was not a very effective means of purification, so a distillation was tried, and the material boiling at 162–193° at 0.2 mm. was collected. After recrystallization from ethanol ($^4/_5$)-isopropyl ether ($^1/_5$) mixture, including filtration of the hot solution, 1.6 g. (14%) of slightly impure triphenylcyclohexylgermane was obtained, m.p. 143–146°.

Anal. Calcd. for $C_{24}H_{26}Ge$: Ge, 18.8. Found: Ge, 19.3, 19.3.

Reaction of triphenylgermane with cyclohexene. Two separate experiments were carried out with 15.2 g. (0.05 mole) of triphenylgermane, 1.0 ml. (0.01 mole) of cyclohexene and 25 ml. of heptane. One reaction was initiated by the addition of 0.3 g. of benzoyl peroxide to the mixture which

---

[4] All reactions were carried out under dry, oxygen-free nitrogen.

[5] Triphenylsilane was prepared by the lithium aluminum hydride reduction of commercial triphenylchlorosilane by Mr. Leonard Moore following the unpublished procedure of J. Curtice.

[6] This procedure was used for the preparation of other alkyllithium compounds by H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949).

[7] H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

[8] Triphenylchlorogermane was prepared from phenylmagnesium bromide and germanium tetrachloride according to the unpublished procedure of Mr. Clare Gerow.

[9] O. H. Johnson and W. H. Nebergall, *J. Am. Chem. Soc.*, **71**, 1720 (1949).

[10] Germanium analyses were done by the method of H. Gilman and C. Gerow, *J. Am. Chem. Soc.*, **77**, 5740 (1955).

was then heated in a 75° bath for 48 hr. A second mixture was irradiated for 48 hr. using an ultraviolet lamp. The following isolation procedure was used on the mixture which had been irradiated. A similar procedure was used for the peroxide-catalyzed reaction product, with like results. Distillation gave, in addition to solvent and unchanged triphenylgermane, 3.0 g. of a solid, b.p. 175–180° at 0.06 mm., which, after recrystallization from a mixture of 150 ml. of absolute ethanol and 50 ml. of isopropyl ether, melted at approximately 150–190°. This latter mixture was lixiviated with hot 80% aqueous ethanol and cooled. The crystals which were deposited melted at 147.0–149.5°, and a mixture with triphenylcyclohexylgermane (m.p. 143–146°) melted at 146.5–148.5°. The infrared absorption spectra confirmed the identity of the two samples. Another portion of the crude solid (m.p. 150–190°) was recrystallized twice from heptane and once from benzene-heptane mixture. The product, which melted at 228–232°, when mixed with authentic tetraphenylgermane (m.p. 232–234°), melted at 231–233°.

Reaction of triphenylgermane with 1,1-diphenylethylene and peroxide. The benzoyl peroxide initiation procedure used with cyclohexene was employed with the substitution of 1.1 ml. (0.0063 mole) of freshly distilled 1,1-diphenylethylene (b.p. 136–140° at 12 mm.) for the cyclohexene. The mixture was heated for 48 hr., and the unchanged triphenylgermane was distilled leaving behind a yellow oil which could not be crystallized with or without the aid of solvents. The oil appeared to be an olefin polymer. The desired product, triphenyl-2,2-diphenylethylgermane, or an isomer, which has been prepared by the addition[11] of triphenylgermylpotassium to 1,1-diphenylethylene, is a readily crystallizable solid which melts at 99.0–99.5°.

Preparation of triphenyl-1-octyltin from triphenyltin chloride and 1-octylmagnesium bromide. 1-Octylmagnesium bromide was prepared from 1.22 g. (0.05 g. atom) of magnesium and 9.7 g. (0.05 mole) of 1-bromooctane in ether. To the filtered Grignard solution was added dropwise a solution of 7.2 g. (0.02 mole) of triphenyltin chloride[12] in ether. The mixture was refluxed for 2 hr. and then was hydrolyzed by the addition of 125 ml. of cold water. The ether layer was separated and dried over magnesium sulfate. Removal of the solvent left a yellow liquid which was crystallized from 150 ml. of ethanol. The yield was 6.3 g. (68%) of crystals which melted at 54.0–54.6°. Another recrystallization raised the melting point to 54.3–55.0°.

Anal. Calcd. for $C_{26}H_{32}Sn$: Sn, 25.6. Found: Sn, 25.8, 26.0.

Reaction of triphenyltin hydride and 1-octene with benzoyl peroxide, ultraviolet or phenylazotriphenylmethane initiation. Three experiments were run using the three sources of radical initiation. In a typical run 23.8 g. (0.068 mole) of triphenyltin hydride,[13] 1.7 ml. (0.01 mole) of 1-octene, 25 ml. of petroleum ether (b.p. 60–70°), and 0.3 g. of benzoyl peroxide were heated to 75° for 24 hr. Another run used ultraviolet irradiation for 4 days at about room temperature in place of the benzoyl peroxide and heat. The third run used 0.3 g. of phenylazotriphenylmethane[14] at room temperature in the dark. In all three cases a white solid was deposited as the reaction progressed. A solution of triphenyltin hydride in petroleum ether remained clear for 2 days when kept in the dark. The white solid was collected by filtration and extracted with hot ethanol. No dissolved material could be isolated from the ethanol, although triphenyl-1-octyltin is very soluble in the hot solvent. Recrystallization of the white solid from chloroform gave crystals melting at 226.0–228.5°. A mixture with authentic tetraphenyltin (m.p. 228.0–228.5°) melted at 226.5–228.5°.

Solvent was distilled from the filtrate from which the tetraphenyltin had originally been isolated. During the distillation the residue changed to a dark gray solid mass, apparently due to disproportionation. Extraction of the solid with hot ethanol failed to dissolve any material suggestive of triphenyl-1-octyltin. The gray solid dissolved in chloroform except for a small amount of black powder which dissolved in hydrochloric acid and appeared to be metallic tin.

Acknowledgment. The authors wish to express their appreciation of the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, for financial assistance.

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA

---

[11] H. Gilman and C. Gerow, *J. Am. Chem. Soc.*, **79**, 343 (1957).

[12] K. A. Kocheshkov, M. M. Nad, and A. P. Aleksandrov, *Ber.*, **67**, 1348 (1934). The material used in this experiment was kindly supplied by Mr. David Miles of this laboratory.

[13] G. Wittig, F. J. Meyer, and G. Lange, *Ann.*, **571**, 167 (1951).

[14] Kindly supplied by Mr. Chester Hamilton and Professor G. S. Hammond.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Stability of an Ether Solution of Methylmagnesium Iodide

HENRY GILMAN AND DONALD L. ESMAY

Received April 25, 1957

Incidental to studies concerned with the stability of some organometallic compounds, it has been observed that an ether solution of methylmagnesium iodide contained in a sealed glass container is essentially unchanged after a period of twenty years.

In connection with studies on the general reactions of organometallic compounds, the stability of Grignard reagents has long been of interest. Previous work in this laboratory[1] indicated that the normalities of diethyl ether solutions of various Grignard reagents, as determined by acid titration,[2] remained essentially unchanged for four months. It was necessary to adequately protect the Gri-

---

[1] H. Gilman and C. H. Meyers, *Ind. Eng. Chem.*, **14**, 243 (1922); **15**, 61 (1923).

[2] H. Gilman, P. D. Wilkinson, W. P. Fishel, and C. H. Meyers, *J. Am. Chem. Soc.*, **45**, 150 (1923).