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Triphenylgermane Addition Reactions

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The reactions of triphenylgermane with a number of organic compounds containing olefinic double bonds, with and without activating functional groups, have been studied. It is shown that, in the absence of solvent and catalyst, triphenylgermane adds to unsaturated carbon bonds. The addition products obtained contained the functional groups unchanged. By means of this reaction some new organogermanium compounds containing functional groups were synthesized.

This paper is concerned with the preparation of functional group-containing organogermanium compounds by means which do not require reactive organometallic intermediates or catalyts. As a result a series of organogermanium compounds, with and without functional groups, were synthesized in a simple and direct manner.

In the germanium series the germanium-hydrogen bond is expected to be less reactive than the correponding tin compounds. This should lead to fewer side effects resulting from exchange and reduction reactions which are frequently noticed with the organotin analog. Fuchs and Gilman[2] have carried out addition reactions with triphenylgermane using octene and cyclohexene, with an inert solvent, a peroxide catalyst or ultraviolet light. Lesbre and co-workers[3a,b] have investigatesd some addition reactions of trialkylgermanes utilizing peroxide or platinum catalysts and in this manner succeeded in preparing several β- or γ-substituted germanium compounds. In addition, they indicated that in the absence of catalyst, trialkylgermanes were added to acrylonitrile, acrylic acid, methyl acrylate, and ethyl acrylate. Subsequent work by the same authors[3c] showed that trialkylgermanes react quantitatively, in the presence of chloroplatinic acid, with acetylenic derivatives, and when phenylacetylene was used the reaction was possible in the absence of catalyst.

We have studied the reaction of triphenylgermane with various olefinic and acetylenic compounds in order to describe in greater detail the nature of this addition reaction. The functional group, when presented in the unsaturated molecule, was either conjugated with the unsaturated linkage or located terminal to it. In this manner, therefore, not only the effect of the Ge—H bond upon the functional group, but also the possibility of introducing functional groups by means of simple addition could be investigated. The following reactions were successfully completed:

$$(C_6H_5)_3GeH + CH_2{=}CHY \longrightarrow (C_6H_5)_3GeCH_2CH_2Y$$

where

$$Y = -C_6H_5,\ -OCOCH_3,\ -CN,\ -CONH_2,$$
$$-COCH_3,\ -COOCH_3,\ -(CH_2)_5CH_3,\ -(CH_2)_2CH_2OH$$

In addition, the expected adducts were obtained by adding triphenylgermane to cyclohexene, 2-methyl-3-butyn-2-ol, and phenylacetylene.

No reducing properties of the triphenylgermane upon the functional groups were observed. Apparently, it is not a prerequisite that the unsaturation be activated by adjacent functional groupings. The results obtained are summarized in Table I.

EXPERIMENTAL

The addition reactions summarized in Table I were carried out in Schlenk tubes equipped with drying tubes and covered at all times by an oxygen-free, inert atmosphere. Infrared spectra of all the products were carried out on a Perkin-Elmer Infracord to check functional groupings and the characteristic absorption band at 1085 cm.$^{-1}$ for the phenylgermanium grouping as previously described.[4] Yields are based upon final recrystallized products. Melting points were taken with a Kofler hot stage. Triphenylgermane was prepared by converting germanium tetrachloride to tetraphenylgermane which in turn was brominated to triphenylbromogermane. The triphenylbromogermane was finally reduced with lithium aluminum hydride.[5]

Triphenyl(2-phenylethyl)germane. A mixture of 2.29 g. (7.5 mmoles) of triphenylgermane and 0.78 g. (7.5 mmoles) of freshly distilled styrene was heated overnight in an oil bath at 120°. The product was recrystallized from acetone and then from a methanol-acetone mixture m.p. 145–146°. The yield was 1.0 g. (40%).

Anal. Calcd. for $C_{26}H_{24}Ge$: Ge, 17.77. Found: Ge, 17.39.

Triphenyloctylgermane. A mixture of 1.12 g. (10 mmoles) of *n*-octene and 3.05 g. (10 mmoles) of triphenylgermane was heated in an oil bath for 5 days at 110–115°. Hexane was added to the reaction mixture which was warmed and allowed to cool. The white crystalline plates that precipitated were recrystallized from hexane and then from methanol, m.p. 62–66°. The yield was 1.2 g. (29%).

Anal. Calcd. for $C_{26}H_{17}Ge$: C, 74.95; H, 7.74; Ge, 17.42. Found: C, 74.54; H, 7.54; Ge, 17.40.

Triphenylstyrylgermane. A mixture of 1.02 g. (10 mmoles) of phenylacetylene and 3.05 g. (10 mmoles) of triphenyl-

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[2] (a) F. Fuchs and H. Gilman, *J. Org. Chem.*, **22**, 1009 (1957); (b) **23**, 911 (1958).

[3] (a) M. Lesbre and J. Satge, *Compt. Rend.*, **247**, 471 (1958); (b) P. Mazeroless and M. Lesbre, *Compt. Rend.*, **248**, 2018 (1959).

(3) (c) M. Lesbre and J. Satge, *Compt. Rend.*, **250**, 2220 (1960).

[4] J. G. Noltes, M. C. Henry, and M. J. Janssen, *Chem. & Ind. (London)*, **1959**, 298.

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

TABLE I. REACTIONS OF TRIPHENYLGERMANE WITH SOME UNSATURATED COMPOUNDS

Unsaturated Compound	Adduct	M.P.
Styrene	$(C_6H_5)_3GeCH_2CH_2C_6H_5$ Triphenyl(2-phenylethyl)germane	145–146
n-Octene	$(C_6H_5)_3Ge(CH_2)CH_3$ Triphenyloctylgermane	64–66[a]
Phenylacetylene	$(C_6H_5)_3GeCH{=}CHC_6H_5$ Triphenylstyrylgermane	146–149
Cyclohexene	$(C_6H_5)_3Ge\overline{CH(CH_2)_4CH_2}$ Triphenylcyclohexylgermane	144–147[a]
2-Methyl-3-butyn-2-ol	$(C_6H_5)_3GeCH{=}CHC(OH)(CH_3)_2$ Triphenyl(3-methyl-3-hydroxybuten-1-yl)germane	90.5–91.5
Vinyl acetate	$(C_6H_5)_3GeCH_2CH_2OCOCH_3$ Triphenyl(2-acetoxyethyl)germane	62–62.5
Acrylonitrile	$(C_6H_5)_3GeCH_2CH_2CN$ Triphenyl(2-cyanoethyl)germane	126–129
4-Pentene-1-ol	$(C_6H_5)_3Ge(CH_2)_4CH_2OH$ Triphenyl(5-hydroxypentyl)germane	51–61
Methyl vinyl ketone	$(C_6H_5)_3GeCH_2CH_2COCH_3$ Triphenyl(2-acetylethyl)germane	144–146
Acrylamide	$(C_6H_5)_3GeCH_2CH_2CONH_2$ Triphenyl(2-carbamylethyl)germane	176–178
Methyl acrylate	$(C_6H_5)GeCH_2CH_2COOCH_3$ Triphenyl(2-methoxycarbonylethyl)germane	60.5–62.0

[a] Fuchs and Gilman[2] report the triphenyl-(*n*-octyl)germane m.p. 72° and the triphenylcyclohexylgermane m.p. 143–146°, 147–149.5°.

germane was heated at 135° for 4 days in an oil bath. The thick viscous oil was chromatographed through a neutral alumina column with hexane. The first fraction to be eluted was recrystallized successively from petroleum ether (b.p. 60–80°), hexane, and finally from ethyl acetate, m.p. 146–149°. The yield was 0.5 g. (12%).

Anal. Calcd. for $C_{26}H_{22}Ge$: C, 76.75; H, 5.46; Ge, 17.85. Found: C, 76.76; H, 5.63; Ge, 17.63.

Triphenylcyclohexylgermane. A mixture of 0.82 g. (10 mmoles) of cyclohexene and 3.05 g. (10 mmoles) of triphenylgermane was heated for 5 days at 60–70° in an oil bath. Addition of hexane to the product yielded a white crystalline product that was recrystallized successively from methanol, cyclohexane, and methanol, m.p. 144–147°. The yield was 1.5 g. (39%).

Anal. Calcd. for $C_{24}H_{26}Ge$: C, 74.53; H, 7.03; Ge, 18.77. Found: C, 74.61; H, 6.78; Ge, 18.68.

Triphenyl(3-methyl-3-hydroxybuten-1-yl)germane. A mixture of 0.84 g. (10 mmoles) of 2-methyl-3-butyn-2-ol and 3.05 g. (10 mmoles) of triphenylgermane was heated 77 hr. at 50–60° in an oil bath. Hexane added to the product mixture yielded a white solid which was recrystallized from butanol and then from methanol, m.p. 90.5–91.5°. The yield was 1.81 g. (49%).

Anal. Calcd. for $C_{23}H_{24}OGe$: C, 71.00; H, 6.17; Ge, 18.67. Found: C, 70.90; H, 6.27; Ge, 18.82.

Triphenyl(2-acetoxyethyl)germane. A mixture of 0.86 g. (10 mmoles) of vinylacetate and 3.05 g. (10 mmoles) of triphenylgermane was heated in an oil bath for 6 hr. at 50–60°. Upon cooling, the mixture solidified. The solid product was crystallized successively from hexane, petroleum ether (b.p. 60–80°), and finally from an acetone-water solution, m.p. 62–62.5°. The yield of white crystals was 2.10 g. (54%).

Anal. Calcd. for $C_{22}H_{22}O_2Ge$: C, 67.64; H, 5.77; Ge, 18.58. Found: C, 67.75; H, 5.77; Ge, 18.70.

Triphenyl(2-cyanoethyl)germane. A mixture of 0.53 g. (10 mmoles) of acrylonitrile and 3.05 g. (10 mmoles) of triphenylgermane was heated in an oil bath at 50–60° for 6 hr. The solid product was taken up in methanol and recrystallized, m.p. 126–129°. The yield was 2.97 g. (83%).

Anal. Calcd. $C_{21}H_{17}NGe$: C, 70.57; H, 5.35; Ge, 20.29. Found: C, 70.55; H, 5.58; Ge, 20.20.

Triphenyl (5-hydroxy-n-pentyl)germane. A mixture of 0.86 g. (10 mmoles) of 4 pentene-1-ol and 3.05 g. (10 mmoles) of triphenylgermane was heated in an oil bath for 4 hr. at 50°. Hexane was added to the cooled product and after warming an oil settled out which crystallized upon standing. This product was then recrystallized again from hexane, m.p. 58–61°. The yield was 1.59 g. (41%).

Anal. Calcd. $C_{23}H_{26}OGe$: C, 70.69; H, 6.70; Ge, 18.58. Found: C, 70.87; H, 7.09; Ge, 18.70.

Triphenyl(2-acetylethyl)germane. A mixture of 0.70 g. (10 mmoles) of methyl vinyl ketone and 3.05 g. (10 mmoles) of triphenylgermane was heated in an oil bath for 18 hr. at 60–70°. Cooling precipitated a mass of white crystals. The filtered product was recrystallized first from petroleum ether (b.p. 60–80°) and finally from methanol, white rectangular plates, m.p. 144–146°. The yield was 2.0 g. (53%).

Anal. Calcd. for $C_{22}H_{22}OGe$: C, 70.45; H, 5.91; Ge, 19.37. Found: C, 70.30; H, 6.16; Ge, 19.39.

The 2,4-dinitrophenylhydrazone precipitated as yellow needles, m.p. 188–192°.

Anal. Calcd. for $C_{28}H_{26}N_4O_4Ge$: C, 60.58; H, 4.71. Found: C, 60.15; H, 4.96.

Triphenyl(2-carbamylethyl)germane. A mixture of 0.47 g. (10 mmoles) of acrylamide and 3.05 g. (10 mmoles) of triphenylgermane was heated in an oil bath for 21 hr. at 50–60°. The solid that separated out of the reaction mixture was filtered and recrystallized from dimethylformamide-water and then from acetone–petroleum ether (b.p. 60–80°) m.p. 176–178°.

Anal. Calcd. for $C_{21}H_{21}OGe$: C, 67.11; H, 5.59; Ge, 19.32. Found: C, 66.96; H, 5.73; Ge, 19.26.

Triphenyl(2-methoxycarbonylethyl)germane. A mixture of 0.86 g. (10 mmoles) of methyl acrylate and 3.05 g. (10 mmoles) of triphenylgermane was heated for 67 hr. at 60–70° in an oil bath. After cooling the resulting oil was taken up and recrystallized from a methanol-water mixture, m.p. 60.5–62.0°. The yield was 1.95 g. (50%).

Anal. Calcd. for $C_{22}H_{22}O_2Ge$: C, 67.62; H, 5.67; Ge, 18.58. Found: C, 67.35; H, 5.91; Ge, 18.42.

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