Anal.[15] Calcd. for $C_{14}H_{14}OSi$: C, 74.5; H, 6.24; mol. wt., 226. Found: C, 74.20, 74.14; H, 6.24, 6.28; mol. wt., 226, 218.

The infrared spectrum determined in a carbon disulfide solution had absorption bands at 3.3, 3.4 and 13.2 μ, indicating the presence of an aromatic C–H, an aliphatic C–H and an *o*-disubstituted benzene, respectively. An absorption band at 13.5 μ, characteristic of a monosubstituted benzene, was absent.

Acknowledgment.—The authors wish to express their appreciation to the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, for financial assistance. They also are grateful to the Institute for Atomic Research, Iowa State College, and Dr. V. A. Fassel and Mr. R. McCord for the actual determination of the spectra.

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[15] The silicon analyses by ignition with sulfuric acid according to the procedure of H. Gilman, B. Hofferth, H. W. Melvin and G. E. Dunn, THIS JOURNAL, **72**, 5767 (1950), gave low erratic results, probably because of the dimethylsilyl group present.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Reactions of Triphenylgermyllithium, Triphenylgermylpotassium and Triphenylgermane with Some Olefins

BY HENRY GILMAN AND CLARE W. GEROW

RECEIVED AUGUST 2, 1956

It has been found that triphenylgermyllithium and triphenylgermylpotassium add to the olefinic linkage in 1,1-diphenylethylene to form 1,1-diphenyl-2-triphenylgermylethane, but neither adds to *trans*-stilbene. In addition, triphenylgermyllithium reacts with octadecene-1 to form triphenyl-*n*-octadecylgermane. With benzalacetophenone, triphenylgermyllithium forms 2-phenyl-2-triphenylgermylethyl phenyl ketone. Triphenylgermane, with peroxide catalyst, reacts with octadecene-1 to give triphenyl-*n*-octadecylgermane and with triphenylallylgermane to give 1,3-bis-(triphenylgermyl)-propane. The authentic preparations of triphenyl-*n*-octadecylgermane and 1,1-diphenyl-2-triphenylgermylethane are given as well as the syntheses of previously unreported triphenylallylgermane and triphenylchloromethylgermane.

In connection with studies in this Laboratory to determine the relative reactivity of triphenylgermylmetallic compounds, to find new methods of introducing germanium into organic molecules and to compare the thermal stabilities of analogous organosilicon and organogermanium compounds, the reactions with olefins were investigated.

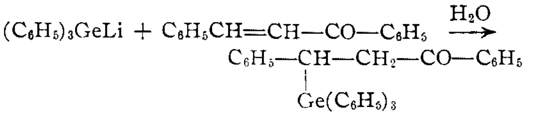
We have found that both triphenylgermylpotassium and triphenylgermyllithium add to the olefinic bond in 1,1-diphenylethylene to give 1,1-diphenyl-2-triphenylgermylethane (I).

$$(C_6H_5)_3GeM + (C_6H_5)_2C{=}CH_2 \xrightarrow{H_2O} (C_6H_5)_2CH{-}CH_2Ge(C_6H_5)_3 \quad (1)$$

I

However, unlike triphenylsilylpotassium[1] and triphenylsilyllithium,[2] neither triphenylgermylpotassium nor triphenylgermyllithium added to the olefinic linkage of *trans*-stilbene. This failure to react with *trans*-stilbene may be due to steric factors because of the larger size of the germanium atom. It is not believed that either triphenylsilylpotassium or triphenylsilyllithium is more reactive than the analogous germanium compounds, because triphenylgermyllithium has been found to add to octadecene-1, while triphenylsilylpotassium fails to react under the same conditions.[3] The reaction of triphenylgermyllithium with olefins is not universally applicable, however, for this reagent was apparently unreactive toward both cyclohexene and octene-1.

With benzalacetophenone, under comparable conditions, triphenylgermyllithium reacted to give a compound believed to be 2-phenyl-2-triphenylgermylethyl phenyl ketone (II).



$$(C_6H_5)_3GeLi + C_6H_5CH{=}CH{-}CO{-}C_6H_5 \xrightarrow{H_2O} C_6H_5{-}\underset{\displaystyle Ge(C_6H_5)_3}{\underset{|}{CH}}{-}CH_2{-}CO{-}C_6H_5 \quad (2)$$

II

Elemental analysis supported this conclusion and infrared analysis indicated the presence of the carbonyl group and the absence of an hydroxyl group. It is not known whether the product was obtained by means of a 1,4- or a 3,4-addition, but it seems altogether probable that 1,4-addition took place.[4] If such is the case, then it is possible to determine to some degree the relative reactivity of triphenylgermyllithium as compared to other organometallic reagents. It has been found that the extent of 1,4-addition to benzalacetophenone might be used as a measure of the relative reactivities of various organometallic reagents.[5] It was found that the more reactive phenylmetallic reagents such as phenylcalcium iodide and phenylpotassium underwent exclusively 1,2-addition to benzalacetophenone. Phenylsodium gave mostly the 1,2-addition product with a small amount of the 1,4-addition product, and phenyllithium gave a larger amount of the 1,4-addition product than did phenylsodium along with 69% of the 1,2-addition product. Phenylmanganese iodide, triphenylaluminum, diphenylzinc and diphenylberyllium gave exclusively the 1,4-addition product. Phenylmagnesium bromide is reported to give the 1,4-addition product exclusively.[6] In the light of this reaction alone, triphenylgermyllithium would be classified as being less reactive than phenyllithium

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[1] H. Gilman and T. C. Wu, THIS JOURNAL, **75**, 234 (1953).

[2] A. G. Brook, K. M. Tai and H. Gilman, *ibid.*, **77**, 6219 (1955).

[3] T. C. Wu, unpublished studies.

[4] For a discussion of 1,4- and 3,4-additions to conjugated unsaturated systems see H. Gilman, "Organic Chemistry," Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 511 and 672.

[5] H. Gilman and R. H. Kirby, THIS JOURNAL, **63**, 2046 (1941).

and as reactive as phenylmagnesium bromide, because no 1,2-addition product was isolated from the reaction of triphenylgermyllithium with benzalacetophenone.

The reactions of triphenylgermylmetallic reagents with olefins and other unsaturated systems[7] indicate a high degree of reactivity for these reagents and allows wide variation in the type of organogermanium compounds which can be synthesized.

The preparation of organosilicon compounds by the free radical addition of silanes to olefins has been reported in a number of publications.[8] The extension of this work to germanes has been made by Fisher, West and Rochow,[9] when they added trichlorogermane to hexene-1 using peroxide catalyst. The mode of addition was not proved but assumed to take place normally to give *n*-hexyltrichlorogermane. A further extension of this work to substituted germanes has been carried out in this Laboratory, and it has been found that triphenylgermane under peroxide catalysis adds to the olefinic linkage in a normal manner to give terminally substituted alkylgermanes.[10] Thus, we found that triphenylgermane reacted with octadecene-1 to give triphenyl-*n*-octadecylgermane and with triphenylallylgermane to give 1,3-bis-(triphenylgermyl)-propane. This latter compound has a melting point only slightly higher than that reported by Smith and Kraus.[11]

The difference in the relative reactivity of triphenylsilane and triphenylgermane is exemplified by the difference in their reaction with triphenylallylgermane. While triphenylgermane gave over 85% yield of the addition product, triphenylsilane did not react under the same conditions.

An authentic specimen of triphenyl-*n*-octadecylgermane was prepared by coupling triphenylchlorogermane with *n*-octadecylmagnesium bromide, and the authentic specimen of 1,1-diphenyl-2-triphenylgermylethane was synthesized by the reaction of triphenylchloromethylgermane with benzhydrylsodium. The previously undescribed triphenylchloromethylgermane was prepared by the action of three moles of phenylmagnesium bromide on chloromethyltrichlorogermane, and triphenylallylgermane was made by the reaction of allylmagnesium bromide with triphenylchlorogermane.

Experimental[12]

Additions of Triphenylgermylmetallic Reagents to Olefins. Triphenylgermylpotassium and 1,1-Diphenylethylene.—A suspension of triphenylgermylpotassium in diethyl ether was prepared from 5.0 g. (0.0082 mole) of hexaphenyldigermane and 1.3 ml. (0.026 g. atom of potassium) of sodium–potassium alloy.[13] To this stirred suspension was added 3.0 g. (0.0165 mole) of 1,1-diphenylethylene dissolved in 30 ml. of dry ether. No heat was evolved, but the color changed to green and then to blue over a period of 1 hr. After stirring 19 hr. the mixture was hydrolyzed by the addition of 100 ml. of water with the color changing from blue to red to white. Filtration then gave 0.6 g. (12%) of hexaphenyldigermane melting over the range 339–345°. The aqueous layer was extracted with ether, the ether extract dried over anhydrous sodium sulfate and the solvent distilled. Addition of petroleum ether to the residue precipitated material which was recrystallized from methanol to yield 0.6 g. (12%) of hexaphenyldigermoxane, m.p. 183–185°. Volume reduction and cooling of the remaining petroleum ether solution and recrystallization from methanol yielded 0.6 g. (15%) of pure 1,1-diphenyl-2-triphenylgermylethane, m.p. 96–97°.

Anal. Calcd. for $C_{32}H_{28}Ge$: Ge, 14.96. Found: Ge, 15.21, 15.26.

Triphenylgermyllithium and 1,1-Diphenylethylene.—A solution of triphenylgermyllithium in ethylene glycol dimethyl ether (GDME) was prepared from 9.6 g. (0.016 mole) of hexaphenyldigermane and about 1 g. (0.14 g. atom) of lithium.[14] To this stirred solution was added 5.8 g. (0.032 mole) of 1,1-diphenylethylene dissolved in 20 ml. of GDME. Heat was evolved and the color changed to brick red and purple over a period of 24 hr. Hydrolysis with water and working up as previously yielded 1.1 g. (11.5%) of hexaphenyldigermane, m.p. 341–343°, 0.8 g. (8%) of impure hexaphenyldigermoxane melting over the range 170–185°, and 2.3 g. (14.8%) of 1,1-diphenyl-2-triphenylgermylethane, m.p. 96–97°.

Triphenylgermyllithium and Octadecene-1.—An ethylene glycol–dimethyl ether solution of triphenylgermyllithium prepared from 7.62 g. (0.02 mole) of tetraphenylgermane was added to 5.04 g. (0.02 mole) of octadecene-1 dissolved in 25 ml. of GDME. After being stirred for 17 hr. the mixture was poured into a saturated ammonium chloride solution. This was extracted with ether, the ether dried and the solvents distilled to leave an oil, to which was added petroleum ether. Cooling the mixture crystallized 0.35 g. (5.5%) of triphenylgermanol (identified by mixed melting point), m.p. 130–132°. Volume reduction and cooling gave triphenyl-*n*-octadecylgermane (0.7 g., 6%), m.p. 74–77°; recrystallized from petroleum ether, 0.4 g. (3.6%), m.p. 75–77°. Its identity was confirmed by mixed melting point and comparison of the infrared spectrum with that of an authentic sample. Although there was a different absorption peak present (760 cm.$^{-1}$) and the elemental analysis was slightly different from that calculated, it is believed that the product was actually triphenyl-*n*-octadecylgermane.

A second run using the same amounts of materials gave 1.0 g. (15.6%) of triphenylgermanol, m.p. 132.5–134.5°, and 3.05 g. (27.3%) of product, m.p. 76–77°. The infrared spectrum was identical with that of the first run and a mixed melting point with authentic triphenyl-*n*-octadecylgermane showed no depression.

Anal. Calcd. for $C_{36}H_{52}Ge$: C, 77.57; H, 9.40; Ge, 13.03. Found: C, 76.65, 76.72; H, 9.52, 9.42; Ge, 13.90, 13.87, 13.84.

Triphenylgermylpotassium and *trans*-Stilbene.—To a stirred, diethyl ether suspension of triphenylgermylpotassium prepared from 5.0 g. (0.0082 mole) of hexaphenyldigermane was added 2.97 g. (0.0165 mole) of *trans*-stilbene dissolved in 50 ml. of dry benzene. This mixture was stirred 14.5 hr. then refluxed an additional 25 hr. Water was then added and the mixture stirred 0.5 hr. and filtered to give 0.3 g. (6%) of hexaphenyldigermane, m.p. 340–343°. The organic layer was separated and the water layer extracted twice with ether. The combined organic portions were dried and the solvents distilled to leave a residue which was crystallized from petroleum ether to give 3.0 g. melting over the range 105–116.5°. Several crystallizations from both ethanol and petroleum ether separated 0.4 g. (7.8%)

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(6) E. P. Kohler, *Am. Chem. J.*, **31**, 642 (1904).

(7) H. Gilman and C. W. Gerow, THIS JOURNAL, **77**, 4675 (1955); **77**, 5740 (1955); *J. Org. Chem.*, **22**, in press (1957).

(8) For further references and for the addition of triphenylsilane to a number of olefins see H. Merten and H. Gilman, THIS JOURNAL, **76**, 5798 (1954); and more recently, D. Seyferth and E. G. Rochow, *J. Org. Chem.*, **20**, 250 (1955).

(9) A. K. Fisher, R. C. West and E. G. Rochow, THIS JOURNAL, **76**, 5878 (1954).

(10) We are indebted to Dr. R. Fuchs for preliminary work on the addition of triphenylgermane to olefins, which will be published at a later date.

(11) F. B. Smith and C. A. Kraus, THIS JOURNAL, **74**, 1418 (1952).

(12) All melting points are uncorrected. Reactions involving organometallic reagents were carried out in an atmosphere of dry, oxygen-free nitrogen. The petroleum ether used in the experimental work described in this publication boiled over the range 60–70° (Skelly B).

(13) H. Gilman and C. W. Gerow, THIS JOURNAL, **77**, 5509 (1955).

(14) H. Gilman and C. W. Gerow, *ibid.*, **77**, 4675 (1955); **77**, 5740 (1955).

of hexaphenyldigermoxane, m.p. 189–193°, and 1.8 g. (60.6%) of *trans*-stilbene melting at 125–127°. No addition product was found.

Triphenylgermyllithium and *trans*-Stilbene.—Using the same procedure as above, two runs were made in GDME using the triphenylgermyllithium from 5.0 g. (0.0082 mole) of hexaphenyldigermane and from 7.62 g. (0.02 mole) of tetraphenylgermane. In neither case was any addition product isolated; 60 and 74%, respectively, of the *trans*-stilbene was recovered and 30% of hexaphenyldigermoxane isolated.

Triphenylgermyllithium and Octene-1.—The triphenylgermyllithium from 7.62 g. (0.02 mole) of tetraphenylgermane in GDME was added to 2.24 g. (0.02 mole) of octene-1 dissolved in GDME. After stirring 16 hr. the mixture was hydrolyzed with water and extracted with ether. The ether solution was dried and the solvents distilled to leave a residue which was dissolved in hot petroleum ether and cooled to give 0.7 g. (11%) of triphenylgermanol (identified by mixed melting point), melting at 132–134°. The petroleum ether was removed by distillation and the residue distilled under 0.03 mm. of pressure with most of the material coming over from 125–130°. The distillate was seeded with triphenylgermane to give 0.7 g. (11%) of triphenylgermane, m.p. 42.5–45°. The residue was dissolved in petroleum ether and cooled to give 0.35 g. of impure hexaphenyldigermoxane melting over the range 150–175°. No addition product was isolated.

Triphenylgermyllithium and Cyclohexene.—The triphenylgermyllithium from 7.62 g. (0.02 mole) of tetraphenylgermane was added to 1.64 g. (0.02 mole) of cyclohexene in GDME. After stirring 13 hr. the mixture was hydrolyzed and worked up as previously to give 0.4 g. (6%) of triphenylgermanol, m.p. 132–134°, and 1.55 g. (26%) of triphenylgermane, m.p. 42–45°. No addition product was isolated.

Reaction of Triphenylgermyllithium with Benzalacetophenone.—The triphenylgermyllithium from 7.62 g. of tetraphenylgermane was added dropwise to 4.2 g. (0.02 mole) of benzalacetophenone dissolved in 25 ml. of GDME. Heat was evolved and the mixture became yellow-green in color. After stirring 12 hr. the now yellow solution was poured into a saturated ammonium chloride solution. Extraction with ether, drying with sodium sulfate and distillation of the solvents left an oil. The oil would not crystallize from petroleum ether, benzene or ethanol, so it was dissolved in ether and set aside. There crystallized 3.4 g. (33%) of addition product melting at 114.5–116.5°. The ether was removed and the remaining oil dissolved in ethanol and cooled to give 0.8 g. (8%) of product melting 116–118°. The two fractions were combined and recrystallized from ether to yield 2.7 g. (26.4%) of addition product, m.p. 119–120°. This product is believed to be 2-phenyl-2-triphenylgermylethyl phenyl ketone.

Anal. Calcd. for $C_{33}H_{28}OGe$: C, 77.23; H, 5.50; Ge, 14.15. Found: C, 77.64, 77.49; H, 5.76, 5.54; Ge, 14.15, 14.17.

Reactions of Triphenylgermane with Olefins. With Octadecene-1.—A solution of 27.5 g. (0.09 mole) of triphenylgermane, 2.52 g. (0.01 mole) of octadecene-1 and 0.32 g. (0.0013 mole) of benzoyl peroxide in 40 ml. of *n*-heptane was maintained at 85° for 17.5 hr. Cooling to room temperature separated 4.9 g. of impure hexaphenyldigermoxane melting over the range 138–170°. Material obtained by further cooling (10°) and the residue after removal of the solvent were combined and vacuum distilled over the range 129–138° (0.1 mm.). The distillate was seeded with triphenylgermane to crystallize 14.2 g. (51%) of slightly impure triphenylgermane, m.p. 43.5–46°. The distillation residue solidified and upon fractional crystallization from petroleum ether gave 1.45 g. of impure hexaphenyldigermoxane and 4.7 g. of addition product. Crystallization twice of the addition product from petroleum ether yielded 3.75 g. (67% based on octadecene-1) of triphenyl-*n*-octadecylgermane, m.p. 75.5–76.5°, identified by mixed melting point and identity of its infrared spectrum with that of the authentic sample. The two impure fractions of hexaphenyldigermoxane were recrystallized from benzene–petroleum ether to yield 5.15 g. (18% based on triphenylgermane), m.p. 182–183.5°, of hexaphenyldigermoxane.

With Triphenylallylgermane.—Using the same procedure as above, 27.5 g. (0.09 mole) of triphenylgermane was allowed to react with 5.53 g. (0.016 mole) of triphenylallylgermane in the presence of 0.32 g. (0.0013 mole) of benzoyl peroxide using 30 ml. of *n*-hexane as the solvent. The solution was refluxed 18.5 hr., then the solvent was removed by distillation and the residue vacuum distilled to give 20.6 g. of impure triphenylgermane melting over the range 35–40°. The residue was dissolved in hot benzene–ethanol and cooled to give 10.05 g. of material melting at 125–127°. This was recrystallized from the same solvent pair to give 9.0 g. (86.5%) of 1,3-bis-(triphenylgermyl)-propane, m.p. 134–136°. An analytical sample melted 135–135.5° (reported 132.5–133.5°).

In two runs using the same procedure as above no addition product was isolated from the attempted reaction of triphenylsilane with triphenylallylgermane.

Preparations of Authentic Samples and Intermediates. Triphenyl-*n*-octadecylgermane.—An ether solution of 0.025 mole of octadecylmagnesium bromide was added rapidly to 7.42 g. (0.025 mole) of triphenylchlorogermane suspended in 25 ml. of ether. When addition was complete the mixture was refluxed 72 hr. and stirred at room temperature for an additional 24 hr. Then 100 ml. of water was added and the mixture was filtered to give 1.3 g. of insoluble material melting over the range 74–82°. This was recrystallized from petroleum ether and ethanol to yield 1.0 g. (13%) of hexatriacontane (mixed melting point) melting at 74–75°. The ether solution was separated from the aqueous layer, dried over anhydrous sodium sulfate and the solvent distilled to leave a residue which was crystallized repeatedly from both ethanol and petroleum ether to give 4.2 g. (30%) of pure triphenyl-*n*-octadecylgermane melting at 79.5–80.5°, and 2.1 g. (15%) of impure material, melting over the range 69–74°, which was not further purified.

Anal. Calcd. for $C_{36}H_{52}Ge$: C, 77.57; H, 9.40; Ge, 13.03. Found: C, 77.47, 77.42; H, 9.45, 9.43; Ge, 12.81, 12.89.

1,1-Diphenyl-2-triphenylgermylethane.—To an ether solution of diphenylmethylsodium, prepared by the cleavage of 2.97 g. (0.015 mole) of benzhydrylmethyl ether by 1 g. (0.044 g. atom) of finely cut sodium over a period of two days,[15] was added an ether suspension of 3.53 g. (0.01 mole) of triphenylchloromethylgermane. There was no immediate evidence of any reaction; however, after being stirred 24 hr. the brown color of the diphenylmethylsodium had changed to light yellow. The mixture was poured into a saturated ammonium chloride solution, the ether layer separated and the aqueous layer washed twice with ether. The combined ether portions were dried and the solvent distilled to leave a residue which was washed with methanol to give 2.84 g. of insoluble material melting over the range 85–110°. From the methanol washings 1.5 g. of unidentified material melting over the range 70–76° crystallized. The insoluble product was refluxed in methanol and filtered hot to give 0.13 g. of insoluble *sym*-tetraphenylethane, m.p. 211.5–213.5°. The solvent was distilled from the filtrate and the residue again refluxed in methanol to give an additional 0.27 g. (total yield 0.4 g., 8%) of *sym*-tetraphenylethane. Removal of the solvent and subsequent crystallization of the residue from benzene–petroleum ether gave 0.7 g. of crude triphenylchloromethylgermane, which after crystallization from petroleum ether yielded 0.5 g. (14%) of pure product, m.p. 117–118°. Concentration of the filtrate resulted in the separation of 1.1 g. of material melting over the range 75–80°. This was crystallized twice from methanol to give 0.44 g. (9%) of 1,1-diphenyl-2-triphenylgermylethane, m.p. 96–97°. A mixed melting point with the products of the reactions of triphenylgermyllithium and -potassium with 1,1-diphenylethylene showed no depression and their infrared spectra were identical.

Triphenylchloromethylgermane.—To 260 ml. of an ether solution of 0.309 mole of phenylmagnesium bromide was added, at a rate sufficient to maintain moderate reflux, 20.5 g. (0.09 mole) of chloromethyltrichlorogermane[16] diluted with an equal volume of ether. With each drop of Grignard reagent a solid separated, necessitating the addition of more ether. When addition was complete the rate of stirring was increased and the mixture was refluxed overnight. Hydrolysis was effected by pouring the mixture into a saturated ammonium chloride solution. The ether

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(15) Adapted from the directions of W. Schlenk and E. Bergmann, *Ann.*, **464**, 1 (1928).

(16) Prepared according to the directions of D. Seyferth and E. G. Rochow, THIS JOURNAL, **77**, 907 (1955).

layer was separated, dried and the solvent distilled to leave 33.2 g. of material melting over the range 95–110°. This product was recrystallized from petroleum ether to yield 24.11 g. (76%) of triphenylchloromethylgermane, m.p. 116–118°. An analytical sample melted at 117.5–118.5°.

Anal. Calcd. for $C_{19}H_{17}GeCl$: Ge, 20.54. Found: Ge, 19.88, 19.67.

Although the germanium analysis is slightly low, it is believed the product is actually triphenylchloromethylgermane; reaction with magnesium followed by hydrolysis gave a 67% yield of triphenylmethylgermane. An attempt, however, to repeat this preparation of triphenylgermylmethylmagnesium chloride failed, as did subsequent attempts to react triphenylchloromethylgermane with lithium in ether and sodium iodide in acetone. The phenyl groups may have a deactivating influence on the carbon–chlorine bond, because Seyferth and Rochow[17] reported no difficulty in preparing trimethylgermylmethylmagnesium chloride.

Triphenylallylgermane.—To 100 ml. of an ether suspension of 51.9 g. (0.147 mole) of triphenylchlorogermane was added 0.212 mole of allylmagnesium bromide[18] in 200 ml. of ether over a period of 1.5 hr. The mixture was stirred overnight at room temperature, then the ether was removed by distillation and the residue heated at 100° for 48 hr. The ether was re-added and 100 ml. of 6 *N* hydrochloric acid was added dropwise while the flask was cooled in an ice-bath. After stirring 2 hr. the mixture was filtered to give 1.6 g. of material melting over the range 210–230°. This material was not further identified. The ether layer was separated, washed with water and dried over anhydrous sodium sulfate. The solvent was then removed by distillation and the residue distilled over the range 194–200° (2.0 mm.) to give 44.3 g. of impure product melting over the range 77–90°. This material was crystallized twice from ethanol to yield 30 g. (59%) of triphenylallylgermane, m.p. 90–91.5°. An analytical sample melted at 90–91°.

Anal. Calcd. for $C_{21}H_{20}Ge$: Ge, 21.05. Found: Ge, 21.24, 21.19.

Acknowledgment.—The authors wish to express their appreciation to the Materials Laboratory, Wright Air Development Center, Wright–Patterson Air Force Base, Ohio, for their financial support of this work. They are grateful also to the Institute for Atomic Research, Iowa State College, for assistance in the infrared determinations.

AMES, IOWA

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[17] D. Seyferth and E. G. Rochow, *J. Org. Chem.*, **20**, 250 (1955).

[18] Prepared according to the directions of H. Gilman and J. H. McGlumphy, *Bull. soc. chim.*, **43**, 1322 (1928).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Allylic Chlorides. XXIII. The 1-Chloro-2-methyl-2-butenes

BY LEWIS F. HATCH AND PAUL R. NOYES

RECEIVED JUNE 26, 1956

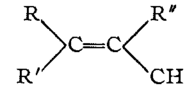
cis- and *trans*-1-chloro-2-methyl-2-butene have been prepared and their infrared spectra and physical properties obtained. Their relative reactivities with sodium ethoxide in ethanol and potassium iodide in acetone were determined. The relative reactivity of these two isomers with iodide ion is compared with the similar activity of *o-* and *p*-methylbenzyl chloride. The similarity between the allyl chloride system and the benzyl chloride system is discussed.

A number of methyl substituted allyl chlorides have been reported previously from this Laboratory: allyl chloride, methallyl chloride,[1,2] *cis-* and *trans*-crotyl chloride,[3] 1-chloro-3-methyl-2-butene[4] and 1-chloro-2,3-dimethyl-2-butene.[5] Both isomers of 1-chloro-2-methyl-2-butene have now been synthesized and their relative reactivities have been determined with sodium ethoxide in ethanol and potassium iodide in acetone. These two isomers complete the series of allylic chlorides with methyl substitution around the carbon–carbon double bond.

1-Chloro-2-methyl-2-butene was first prepared in 1926 by Seyer and Chalmers[6] and since that time by several others using various methods of synthesis.[7–9] In all of these preparations no mention was made of geometrical configuration, but apparently the *cis* isomer was formed. Tamale and co-workers[10] prepared 1-chloro-2-methyl-2-butene from the corresponding alcohol by use of phosphorus trichloride, but the configuration of the alcohol was not reported. The relative reactivity (9.18) of their material with iodide ion indicates that it contained about 10% of the *trans* isomer (Table I).

TABLE I

THE RELATIVE REACTIVITY OF VARIOUS METHYL SUBSTITUTED ALLYLIC CHLORIDES WITH POTASSIUM IODIDE AND WITH SODIUM ETHOXIDE,



	Compound		Iodide ion	Ethoxide ion
R	R′	R″		
H	H	H	1.00[a]	1.00[b]
CH_3	H	H	1.56[c]	4.43[c]
H	H	CH_3	1.58[a]	1.03[b]
CH_3	H	CH_3	5.27[d]	3.94[d]
H	CH_3	H	8.35[c]	5.14[c]
CH_3	CH_3	H	28.1[e]	
H	CH_3	CH_3	41.8[d]	4.36[d]
CH_3	CH_3	CH_3	150[f]	

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