The Chloroplatinic Acid Catalyzed Addition of Trimethylgermanium Hydride to Dienes[1]

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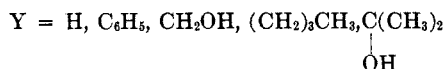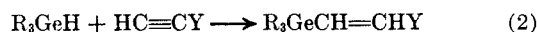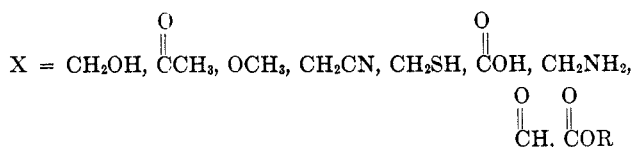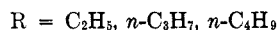
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The chloroplatinic acid catalyzed addition of trimethylgermanium hydride to allene, 1,3-butadiene, cyclopentadiene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, 1,3-cyclooctadiene, 1,5-cyclooctadiene, 4-vinylcyclohexene, and bicyclo[2.2.1]heptadiene-2,5 has been studied. Structures and configurations of the adducts have been assigned on the basis of infrared and nuclear magnetic resonance spectroscopy as well as chemical degradation. The course of the addition to some of the dienes is discussed in terms of "coordination control." A trimethylgermanium–platinum hydride complex is postulated as an intermediate in the isomerization of 1,5-cyclooctadiene to 1,3-cyclooctadiene.
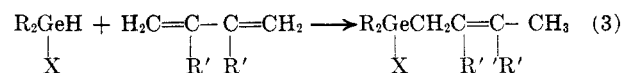
The addition of organogermanium hydrides to unsaturated compounds has been investigated previously, particularly by Lesbre and co-workers.[4-7] Results are summarized in eq 1 and 2.

$$R_3GeH + CH_2=CHX \longrightarrow R_3GeCH_2CH_2X + R_3GeCHCH_3 \quad (1)$$
$$\underset{X}{}$$
$$(\text{trace})$$

$$R = C_2H_5,\ n\text{-}C_3H_7,\ n\text{-}C_4H_9$$

$$X = CH_2OH,\ \overset{O}{\overset{\|}{C}}CH_3,\ OCH_3,\ CH_2CN,\ CH_2SH,\ \overset{O}{\overset{\|}{C}}OH,\ CH_2NH_2,$$
$$\overset{O}{\overset{\|}{C}}H,\ \overset{O}{\overset{\|}{C}}OR$$

$$R_3GeH + HC\equiv CY \longrightarrow R_3GeCH=CHY \quad (2)$$
$$Y = H,\ C_6H_5,\ CH_2OH,\ (CH_2)_3CH_3, \underset{\underset{OH}{|}}{C(CH_3)_2}$$

Gilman and Fuchs[8] added triphenylgermanium hydride to 1-octene, cyclohexane, and 1,1-diphenylethene under free-radical conditions. Lesbre and co-workers added organogermanium halohydrides to a number of olefins.[9] The only examples of additions to dienes are reported in the work of Mironov and co-workers, who added trichlorogermanium hydride to 1,3-butadiene, 1-methyl-1,3-butadiene, 2-methyl-1,3-butadiene and cyclopentadiene,[10-13] and in that of Satgé and Massol who added alkylhalogermanium hydrides to 1,3-butadiene and 2,3-dimethyl-1,3-butadiene.[14] The latter showed that 1,4 addition (eq 3) occurred with these dienes.

$$R_2GeH + H_2C=C-C=CH_2 \longrightarrow R_2GeCH_2C=C-CH_3 \quad (3)$$
$$\underset{X}{} \underset{R'\ R'}{} \qquad \underset{X}{} \underset{R'\ R'}{}$$

$$R = C_2H_5,\ C_3H_7$$
$$X = Cl,\ Br$$
$$R' = H,\ CH_3$$

dienes. There has been, however, no report of work on the addition of triorganogermanium hydrides to dienes. Thus, a study of the addition of trimethylgermanium hydride to a variety of dienes was carried out in order to ascertain the course and stereochemistry of these reactions.

Results

The addition of trimethylgermanium hydride to several dienes was carried out in sealed ampoules at appropriate temperatures in the presence of chloroplatinic acid. Product mixtures were analyzed by gas-liquid partition chromatography (glpc) and the structures elucidated by a combination of infrared and nmr spectroscopy, as well as chemical degradation. The structures of all the products isolated are given in Chart I. Yields, product distribution, and analytical data are listed in Table I. Characteristic infrared bands are found in Table II, and nmr data, including chemical shifts in τ units, coupling constants in cycles per second, and assignments, are found in Table III.

Allene.—Allene provided, in 47.5% yield, a mixture containing allyltrimethylgermanium (1, 60.5%) and prop-2-en-2-yltrimethylgermanium (2, 39.5%). Compound 1 was identified by its infrared and nmr spectra, as well as its physical constants which were in agreement with those reported previously.[14] Compound 2 was identified by its infrared spectrum which showed bands at 3045, 1605, and 915 cm^{-1}, characteristic of vinylgermanium compounds[15] and by its nmr spectrum: vinyl proton multiplets at τ 5.23 and 5.48 ($J = 1.2$ cps) and the methyl group as a partially resolved triplet at τ 8.2 ($J = 1.4$ cps) as well as the trimethylgermanium singlet at τ 9.8. The reaction mixture also afforded, in 19% yield, a higher boiling compound which was not identified; however, it is postulated to be a polymer of 2.

1,3-Butadiene.—The products 3 and 4 were obtained in 65% yield, in the ratio 40:60. *trans*-Crotyltrimethylgermanium (3) had the characteristic strong out-of-plane deformation of a *trans*-disubstituted double bond at 960 cm^{-1}. Its nmr spectrum showed the vinyl

(4) M. Lesbre and J. Satgé, *Compt. Rend.*, **247**, 471 (1958).
(5) J. Satgé, *Ann. Chim.* (Paris), **6**, 519 (1961).
(6) M. Lesbre and J. Satgé, *Compt. Rend.* **250**, 2220 (1960).
(7) M. Lesbre, J. Satgé, and M. Massol, *ibid.*, **256**, 1548 (1963).
(8) H. Gilman and R. Fuchs, *J. Org. Chem.*, **22**, 1009 (1957).
(9) M. Lesbre, J. Satgé, and M. Massol, *Compt., Rend.*, **250**, 2220 (1960).
(10) V. F. Mironov, T. K. Gar, and L. A. Leites, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1387 (1962).
(11) V. F. Mironov and T. K. Gar, *ibid.*, 578 (1963).
(12) V. F. Mironov and T. K. Gar, *Dokl. Adad. Nauk SSSR*, **152**, 1111 (1963).
(13) A. D. Petrov, V. F. Mironov, and I. E. Golgy, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1146 (1956).
(14) J. Satgé and M. Massol, *Compt. Rend.*, **261**, 170 (1965).
(15) R. Noel-Mathis, P. Mazerolles, and F. Mathis, *Bull. Soc. Chim. France*, 1955 (1961).

TABLE I

TABLE I
PREPARATIVE, PHYSICAL, AND ANALYTICAL DATA ON TRIMETHYLGERMANIUM HYDRIDE–DIENE ADDUCTS

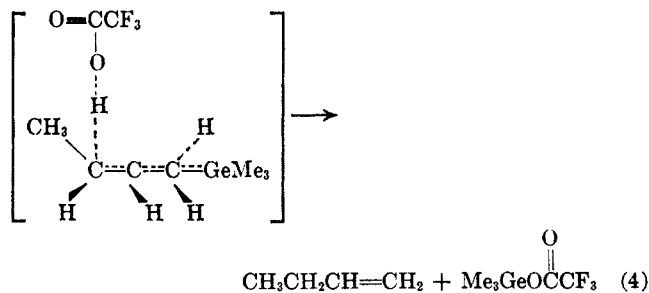| Diene	Temp, °C	Time, hr	Bp, °C (mm)	Yield, %	Compd	%	n^{25}D	Formula	Calcd C	Calcd H	Found C	Found H
H₂C=C=CH₂[b]	115	8.5	97–98 (760)	47.5	1[c]	60.5	1.4278	C₆H₁₄Ge	45.40	8.83	45.65	9.00
					2	39.5	1.4260	C₆H₁₄Ge	45.40	8.83	45.60	8.92
H₂C=C—C=CH₂[d] H H	140	10	125–127 (760)	65	3	40	1.4375	C₇H₁₆Ge	48.67	9.27	48.49	9.32
					4	60	1.4430	C₇H₁₆Ge	48.67	9.27	48.83	9.48
(cyclopentadiene)[e]	175	5	52–54 (15)	25	5[f]	62.7	1.4657	C₈H₁₆Ge	52.00	8.67	52.10	8.84
					6	37.3	1.4662	C₈H₁₆Ge	52.00	8.67	52.10	8.84
(cyclohexadiene)[g]	140	10	38–39 (1.5)	60	7	100	1.4795	C₉H₁₈Ge	54.38	9.06	54.36	9.11
(cyclohexadiene)[g]	140	10	34 (1.0)	49	7	100		C₉H₁₈Ge	54.38	9.06	54.36	9.11
(cyclooctadiene)[h]	160	10	78–78.5 (0.75)	30	8	100	1.4869	C₁₁H₂₂Ge	58.25	9.70	58.40	9.54
(cyclooctadiene)[h]	150	10	47.5 (0.2)	42	8	100		C₁₁H₂₂Ge	58.25	9.70	58.40	9.54
(vinylcyclohexene)[h]	150	8	93–94 (0.3)	47	9	100	1.4756	C₁₁H₂₂Ge	58.25	9.70	58.46	9.90
(norbornadiene)[h]	140	8	83–84 (1.7)	80	10[i]	75	1.4834	C₁₀H₁₈Ge	56.98	8.54	56.82	8.77
					11[i]	15		C₁₀H₁₈Ge	56.98	8.54	56.82	8.77
					12[i]	10		C₁₀H₁₈Ge	56.98	8.54	56.82	8.77

[a] All products were separated on a 20 ft × ³/₈ in. silicone nitrile (GE XF 1150) column on Chromosorb P (60–80 mesh).   [b] 100% excess diene.   [c] All physical constants were in accord with those reported in ref 13.   [e] 1:1 ratio, diene to hydride.   [f] All physical constants in accord with those reported in ref 10.   [g] 50% excess diene.   [h] 10% excess diene.   [i] Based on trimethylgermanium proton peak areas in nmr spectrum.

TABLE II
INFRARED SPECTRAL DATA FOR THE TRIMETHYLGERMANIUM HYDRIDE–DIENE ADDUCTS[a,b]

Adduct	Vinyl C–H str	C=C str	C–H sym def CH₃–Ge	cis-C=C out of plane	CH₃–Ge rocking	Other
1	3065 (m)	1630 (s)	1235 (s)		825 (s)	987 (m),[c] 890 (s)[d]
2	3045	1605 (vw)	1235 (s)		825 (s)	915 (s)[d]
3	3013 (m)	1650 (w)	1235 (s)			960 (s)[e]
4	3012 (m)	1645 (m)	1235 (s)	720 (m)	825 (s)	
5	3020 (m)	1595 (m)	1235 (s)		825	
6	3050 (m)	1595 (m)	1235 (s)	715 (m)	825	
7	3013 (s)	1630 (m)	1235 (s)	715 (m)	825	
8	3022 (m)	1650 (w)	1235 (s)	700 (m)	825	
9	3020 (m)	1650 (w)	1235 (s)	710 (m)	825	
10–12	3040 (m)	1570 (w)	1235 (s)	720 (s)	825 (s)	1335 (m)[f]

[a] Neat liquid.   [b] Bands in cm⁻¹.   [c] Vinyl C–H out-of-plane deformation.   [d] =CH₂ out-of-plane deformation.   [e] trans-HC=CH out-of-plane deformation.   [f] cis-HC=CH in-plane deformation.

protons as a multiplet at τ 4.70, a multiplet at 8.41, and the trimethylgermanium singlet at 9.90 in the ratio 2:5:9, respectively. Compound **4** had an infrared spectrum which showed a band at 720 cm⁻¹, characteristic of the out-of-plane deformation for a *cis*-disubstituted double bond. The nmr spectrum had vinyl protons as a multiplet at τ 4.75, a multiplet at 8.46, as well as a trimethylgermanium singlet at 9.87 in the ratio 2:5:9. The complexity of the nmr spectra of **3** and **4** made it impossible to determine coupling constants for the *cis* and *trans* isomers by simple inspection; however, the electrophilic cleavage reaction of the mixture of *cis* and *trans* isomers with trifluoroacetic acid gave 1-butene as the only cleavage product. The formation of 1-butene can be rationalized in terms of an SE2' mechanism previously observed for the analogous crotyltrimethyltins[16] (eq 4).

(16) H. G. Kuivila and J. A. Verdone, *Tetrahedron Letters*, **No. 3**, 119 (1964).

$$
\left[\begin{array}{c} O=CCF_3 \\ | \\ O \\ | \\ H \\ | \\ CH_3 \quad \quad H \\ \diagdown \quad | \quad \diagup \\ C=C=C=GeMe_3 \\ \diagup \quad \diagdown \diagdown \\ H \quad H \ H \end{array} \right] \longrightarrow
$$

$$
CH_3CH_2CH=CH_2 + Me_3GeO\overset{O}{\overset{\|}{C}}CF_3 \quad (4)
$$

Cyclopentadiene.—The products **5** and **6** were obtained in 25% over-all yield, and in the ratio 67.7:37.3. Cyclopent-1-en-1-yltrimethylgermanium (**5**) was characterized by its infrared spectrum which showed bands at 3020 and 1595 cm⁻¹ and its nmr spectrum which had a vinyl proton multiplet at τ 4.31 ($J = 2.1$ cps) and multiplets at 7.75 and 8.20, as well as the trimethylgermanium singlet at 9.84 with integrated area ratios

Table III

NMR Spectral Data on the Trimethylgermanium Hydride–Diene Adducts[a,b]

Adduct	Concn in CCl₄, %	a	b	c	d	e	f	g	h	i	J_{a-b}	J_{a-c}	J_{b-c}	J_{c-b}
1	Neat	5.48 (m)	5.23 (m)	4.35 (6)	8.42 (2)	9.88 (1)					1.0	15	11	8.0
2	25	4.67 (m)	5.04 (m)	8.2 (3)	9.80 (1)	9.90 (2)					1.2	1.4	1.4	
3	25	4.70 (m)	8.41 (m)	4.70 (m)	8.41 (m)	9.87 (1)	9.87 (1)							
4	25	4.75 (m)	8.46 (m)	4.75 (m)	8.46 (m)	9.84 (1)	9.84 (1)				2.1			
5	35	4.31 (m)	7.75 (m)	8.2 (m)	8.2 (m)	7.90 (m)	9.90 (m)	9.90 (1)						
6	40	4.45 (m)	4.45 (m)	7.90 (m)	7.90 (m)	8.3 (m)	9.87 (1)	9.87 (1)						
7	Neat	4.40 (m)	4.40 (m)	8.06 (m)	8.3 (m)	8.3 (m)	9.90 (1)	9.90 (1)						
8	20	4.35 (m)	4.35 (m)	7.85 (m)	8.45 (m)	8.45 (m)	8.45 (m)	9.90 (1)						
9	Neat	4.45 (2)	4.45 (2)	8.0 (m)	8.67 (m)	8.67 (m)	8.67 (m)	9.25 (m)	9.88 (1)					
10–12	Neat	4.13 (3)c	4.13 (3)c	8.5 (m)	7.12 (m)c	7.12 (m)c	8.5 (m)	8.5 (m)	9.96 (1)d					

[a] See Chart I for structure and proton designation. [b] Values are reported in τ units and measured to the center of each multiplet. J values are in cps. [c] $J_{ad} = J_{bc} \cong 3.0$ cps. [d] Trimethylgermanium singlet for 10. [e] Trimethylgermanium singlet for 11 and 12.

Chart I
Trimethylgermanium Hydride–Diene Adducts

Structures **1**–**12** with proton designations (a–i) and GeMe₃ / Me₃Ge groups as labeled:

- **1** Me₃Ge—CH₂C=C(H_a)(H_b), H_c
- **2** CH₃(c)–C=C(H_a)(H_b), Me₃Ge(d)
- **3** Me₃GeCH₂–C=C(H_a)(CH₃ b), H_c
- **4** Me₃GeCH₂–C=C(CH₃ b)(H_a), H_c
- **5** cyclopentadiene ring, Me₃Ge(e)
- **6** cyclopentene ring with Me₃Ge(f)
- **7** cyclohexene ring, GeMe₃(f)
- **8** cyclooctene ring, GeMe₃(f)
- **9** fused ring, GeMe₃(h)
- **10** bicyclic, GeMe₃(h)
- **11** norbornene, GeMe₃(i)
- **12** bicyclic, GeMe₃(i)

1:4:2:9, respectively. Cyclopent-2-en-1-yltrimethyl-germanium (6) had an infrared spectrum with bands at 3050, 1595, and 715 cm⁻¹, and an nmr spectrum with a vinyl proton multiplet at τ 4.45, a multiplet at 7.90, and the trimethylgermanium singlet at 9.90 with integrated area ratios 2:5:9. The mixture of 5 and 6 was treated with trifluoroacetic acid; 6 reacted completely while 5 did not react under the condition employed. This substantiates the assignment of 6 as the allylic germanium compound.

1,3-Cyclohexadiene.—The product obtained in 60% yield consisted of one isomer, cyclohex-2-en-1-yltrimethylgermanium (7) (glpc). The infrared spectrum of 7 had bands at 3013, 1630, and 715 cm⁻¹, while the nmr spectrum showed a vinyl proton multiplet at τ

4.40. A multiplet at τ 8.07 was assigned to the methylene group α to the double bond[17] and the remaining protons, a multiplet at τ 8.30, and the trimethylgermanium singlet at 9.87. The integrated area ratio was 2:2:5:9, consistent with the assigned structure. Compound 7 reacted exothermally with trifluoroacetic acid to give cyclohexene and trimethylgermanium trifluoroacetate.

1,4-Cyclohexadiene.—The product formed in 40% yield was identical with the product (infrared and nmr) formed in the reaction of 1,3-cyclohexadiene and trimethylgermanium hydride. A careful examination of recovered diene by glpc indicated the presence of 1,3-cyclohexadiene. This leads to the conclusion that 1,4-cyclohexadiene isomerizes to 1,3-cyclohexadiene, which then reacts with the hydride to form 7.

1,3-Cyclooctadiene.—The product which was obtained in 30% yield was found to be homogeneous by glpc. It was characterized as 8 by its infrared spectrum which showed bands at 3020, 1650, and 700 cm^{-1} and by its nmr spectrum which had a vinyl proton multiplet at τ 4.35 and a multiplet at 7.85 which was assigned to the allylic methylene group. The remaining peaks consisted of a multiplet at τ 8.45 due to the other ring methylene protons and a singlet at τ 9.90 due to the methyl groups on germanium. The integrated area ratios were 2:2:9:9. Compound 8 reacted exothermally with trifluoroacetic acid to give cyclooctene and trimethylgermanium trifluoroacetate.

1,5-Cyclooctadiene.—The product formed in 42% yield was identical with the product (infrared and nmr) formed in the reaction of 1,3-cyclooctadiene and trimethylgermanium hydride. In an experiment to substantiate the isomerization of 1,5- to 1,3-cyclooctadiene, it was found that, in the presence of catalytic amounts of chloroplatinic acid and trimethylgermanium hydride, 1,5-cyclooctadiene was isomerized to 1,3-cyclooctadiene (Table IV).

TABLE IV

ISOMERIZATION OF 1,5-CYCLOOCTADIENE TO 1,3-CYCLOOCTADIENE

Expt[a]	Contents	Results[b]
1	1,5-Cyclooctadiene	No change
2	1,5-Cyclooctadiene and a catalytic amount of chloroplatinic acid	No change
3	1,5-Cyclooctadiene and a catalytic amount of trimethylgermanium hydride and chloroplatinic acid	A mixture of 1,3- and 1,5-cyclooctadiene was present

[a] The compounds were heated at 160° for 9 hr. [b] Analyzed by glpc on an 11-ft 17% silicone nitrile on Chromosorb P column. 1,3-Cyclooctadiene was collected and identified by comparison of its infrared spectrum with that of an authentic sample.

4-Vinylcyclohexene.—The 4-vinylcyclohexene reaction yielded one pure product (glpc) in 46.7% yield. It was identified as 9 by its infrared spectrum which showed bands at 3020 and 1650 cm^{-1}. The absence of bands at 880–920 cm^{-1} as well as at 980 cm^{-1} indicated that the trimethylgermanium hydride added to the exocyclic double bond. Its nmr spectrum had a vinyl proton multiplet at τ 4.45; a multiplet at 8.0 was

(17) L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, The Macmillan Co., New York, N. Y., 1959, Chapter 7.

assigned to the two methylene groups α to the double bond.[17] A multiplet at τ 9.25 was assigned to the methylene protons on the carbon bearing the trimethylgermanium group. The remaining protons were a multiplet at τ 8.67 and the trimethylgermanium singlet at 9.88. The integrated area ratios were 2:4:2:5:9.

Compound 9 was unreactive toward trifluoroacetic acid even after heating at 100° overnight in tetrahydrofuran. This indicates that acid cleavage of the carbon–germanium bond in unsaturated compounds occurs much more readily if the bond is in the allylic position than if it is not.

Bicyclo[2.2.1]heptadiene-2,5.—The reaction produced, in 80% yield, three components which could not be separated by glpc. Nmr spectroscopy could be used, however, to determine the ratio of products.[18] The *endo* trimethylgermanium group (10) was upfield owing to the magnetically anisotropic double bond, while the *exo* group (11) was shifted to lower field and had the same chemical shift as that in 12.

10, *endo*   11, *exo*
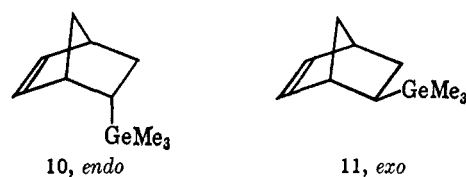
The fraction of nortricyclene isomer 12 was determined by first measuring the area of the trimethylgermanium singlets (*exo* and *endo*) in the norbornene derivatives. The mixture (10, 11, and 12) was then hydrogenated and the areas of the trimethylgermanium singlets in the norbornane derivatives (*exo* and *endo*) were measured. The *exo* and *endo* trimethylgermanium singlets had exchanged relative positions due to elimination of the magnetically anisotropic double bond. The difference in the peak areas for the *endo*-norbornane and *endo*-norbornene indicated the presence of 10% of 12.

Discussion

The utility of platinum and chloroplatinic acid as catalysts for the addition of silanes[18-24] and germanium hydrides to olefins is well recognized. A careful study by Speier and Ryan[21] has revealed that extensive exchange of hydrogen occurs in the addition of trichlorosilane-*d* to olefins and that considerable isomerization of the olefin may occur. They postulated that these processes occur through a series of additions and eliminations of a silane–platinum complex to the olefin. A similar mechanism was proposed by Chalk and Harrod[25] for the hydrosilation of olefins in the presence of group VIII metal complexes. Our results indicate that a similar mechanism may be involved in the addition of germanium hydrides to dienes. This would account for the formation of the 1,3-dienes during the

(18) H. G. Kuivila and C. R. Warner, J. Org. Chem, **29**, 2845 (1964).
(19) J. L. Spier, J. A. Webster, and G. H. Barnes, J. Am. Chem Soc., **79**, 974 (1957).
(20) J. C. Saam and J. L. Spier, ibid., **80**, 4104 (1958).
(21) J. C. Saam and J. L. Spier, ibid., **83**, 1351 (1961).
(22) J. W. Ryan and J. L. Spier, ibid., **86**, 895 (1964).
(23) R. A. Benkeser, M. L. Burrows, L. E. Nelson, and J. F. Swisher, ibid., **83**, 4385 (1961).
(24) T. G. Selin and R. West, ibid., **84**, 1863 (1962).
(25) A. J. Chalk and J. F. Harrod, ibid., **87**, 16 (1965).

course of addition of trimethylgermanium hydride to 1,4-cyclohexadiene and 1,5-cyclooctadiene. The absence of product derived directly from these two unconjugated dienes indicates that they undergo isomerization more rapidly than they undergo germanium hydride addition, and that the conjugated diene may undergo addition more rapidly than the unconjugated diene.

The chloroplatinic acid catalyzed addition of trimethylsilane to norbornadiene yields 5-trimethylsilylnorbornene containing the *endo* and *exo* isomers in a ratio of about 2.5:1.[18] This result, which is in contrast to that observed in most other additions to norbornadiene, was attributed to the functioning of "coordination control," *i.e.*, the ability of the *endo* side of the diene to function as a bidentate ligand. The addition of trimethylgermanium hydride is even more strongly biased (5:1) in favor of *endo* addition, presumably for the same reason. Another intimation that coordination can play a role in directing the course of addition to dienes is provided by the example of butadiane. The product mixture contained 60% of *cis*- and 40% of *trans*-crotyltrimethylgermanium (**3** and **4**, respectively). In this instance "coordination control" would tend to hold the diene in the cisoid conformation, which would lead to the *cis*-crotyltrimethylgermanium by a 1,4 addition. It is clear from these examples that this factor can affect the course of the addition of hydrides to dienes substantially, and may be fairly common when atoms with vacant d orbitals are involved.

Perhaps the most unexpected product obtained in this investigation was cyclopent-1-en-1-yltrimethylgermanium (**5**) which was obtained in nearly twice the yield of **6**, the product resulting from 1,4 addition (or 2,1 addition), in the reaction with cyclopentadiene. A rationale for the formation of **5** can be found by assuming the formation of a bis adduct of the trimethylgermanium hydride–platinum complex as shown in eq 5, in which the complex is given a structure analogous to that used for the silane case by Ryan and Speier.[22]

(5)
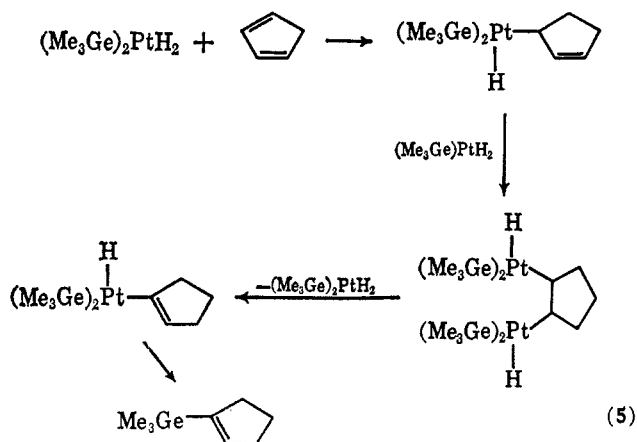
Elimination of complex in the appropriate direction, followed by formation of the germanium–ring carbon bond yields **5**.

It is noteworthy that 4-vinylcyclohexene did not undergo isomerization of the endocyclic double bond into conjugation with the exocyclic vinyl group. This is consistent with the observation of Speier and Ryan[21]

that terminal double bonds undergo hydrosilation rapidly and irreversibly.

Experimental Section

Boiling points are uncorrected. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were obtained on a Perkin-Elmer Model 337 grating spectrophotometer (sodium chloride optics). The nmr spectra were recorded on a Varian A-60 instrument with tetramethylsilane as an internal standard. The glpc analyses were carried out with Aerograph A-70 and F & M Model 300 instruments. Peak areas were used to calculate percentages of the isomeric products.

Materials.—Allene (Matheson Co.) was 98.5% pure with 1.5% propylene as the only impurity noted (glpc on a 15 ft × 0.25 in dimethylsulfolane column on firebrick at room temperature). Dicyclopentadiene (Eastman Kodak) was cracked to give cyclopentadiene. 1,3-Cyclohexadiene (Aldrich Chemical Co.) was used without purification. 1,3-Cyclooctadiene, 1,5-cyclooctadiene, and 4-vinylcyclohexene-1, a gift from Cities Service, were also used without purification. 1,4-Cyclohexadiene was prepared by the method of Bothner-By.[26] Bicycloheptadiene, a gift from Shell Development, was distilled before use. The chloroplatinic acid was purchased from Fisher Scientific Co. and was used as a *ca* 0.1 *N* solution in absolute ethanol. The germanium tetrachloride was purchased from the Eagle–Picher Co. and a generous amount of tetraphenylgermanium was a gift from Dr. G. J. M. van der Kerk, Institute for Organic Chemistry T. N. O., Utrecht, Holland.

Preparation of Trichlorophenylgermanium.[27]—To 15.3 g (0.071 mole) of germanium tetrachloride was added 6.8 g (0.0178 mole) of tetraphenylgermanium in a sealed tube. The sealed tube was heated in a bomb at 300° for 36 hr. Distillation gave 13.74 g [77%, bp 84–86 (1.8 mm)] of product.

Preparation of Trimethylphenylgermanium.—To 0.372 mole of methylmagnesium bromide in 500 ml of anhydrous diethyl ether was added, with cooling, 15.88 g (0.062 mole) of trichlorophenylgermanium dissolved in 100 ml of anhydrous diethyl ether. Addition was complete in 2 hr; the mixture was stirred overnight. The excess Grignard reagent was hydrolyzed with a saturated ammonium chloride solution. The ether layer was separated and washed thrice with cold water, then dried over magnesium sulfate. Distillation gave 7.6 g [67%, bp 82–85° 20 mm] of product. By not cooling the Grignard upon addition of the trichlorophenylgermanium and refluxing the mixture for 9 hr, yields were increased to 80%.

Preparation or Trimethylgermanium Bromide.—To 7.6 g (0.039 mole) trimethylphenylgermanium dissolved in 15 ml of ethyl bromide was added dropwise over a 1-hr period 6.25 g (0.039 mole) bromine dissolved in 15 ml of ethyl bromide. Distillation gave 7.63 g, 98%, bp 113–115° (760 mm), n^{25}D 1.4688 [lit.[5] bp 113–114° (760 mm), n^{20}D 1.4713], of product.

Preparation of Trimethylgermanium Hydride.—In a flask equipped with a stirrer, dropping funnel, and distilling head was placed 0.735 g (0.0193 mole) of lithium aluminum hydride suspended in 25 ml of 1,2-dimethoxyethane. To this solution was added 7.63 g (0.0386 mole) of trimethylgermanium bromide dissolved in 15 ml of 1,2-demethoxyethane. After addition was complete, the flask was heated to 70° with a wax bath; the product was distilled to give 3.51 g (77%), bp 26° (760 mm).

Reaction of Trimethylgermanium Hydride with Bicyclo[2.2.1]-heptadiene-2,5.—To 3.51 g (0.029 mole) of trimethylgermanium hydride was added 2.9 g (0.0315 mole) of bicyclo[2.2.1]heptadiene-2,5 in a glass ampoule along with 0.3 ml of a 0.1 *M* chloroplatinic acid solution (ethanol). The ampoule was sealed at 78° and then heated in a bomb at 140° for 8 hr. Distillation gave 4.89 g [80%, bp 82–84° (1.7 mm)] of product. Glpc (4 ft × ¼ in, 20% Apiezon L on Chromosorb P column, 60–80 mesh) indicated one component; nmr spectroscopy, however, showed the presence of three components: **10** (75%), **11** (15%), and **12** (10%).

Attempted Reaction of 4-Ethyl(2′-trimethylgermanyl)cyclohexene-1,9 with Trifluoroacetic Acid.—To 0.4453 g (1.97 × 10⁻³ mole) of 4-ethyl(2′-trimethylgermanyl)cyclohexene-1 was added 0.225 g (1.97 × 10⁻³ mole) of trifluoroacetic acid. Upon

(26) A. P. Krapcho and A. Bothner-By, *J. Am. Chem. Soc.*, **81**, 3665 (1959).

(27) R. Schwarz and E. Schmaisser, *Ber.*, **69**, 579 (1936).

mixture of the two components only a color change was evident, but no reaction had taken place. Glpc analysis (4 ft × ¹/₄ in, 20% Apiezon L on Chromosorb P column, 60–80 mesh) indicated that only starting materials were present. A few drops of tetrahydrofuran were added and a homogeneous solution resulted. This solution was heated on a steam bath overnight; glpc, however, indicated that no reaction had taken place.

Reaction of cis- and trans-Crotyltrimethylgermanium with Trifluoroacetic Acid.—In a flask equipped with a septum and a gas outlet to a Dry Ice–acetone trap was placed 0.141 g (8.2 × 10⁻⁴ mole) of cis- and trans-crotyltrimethylgermanium (60% cis, 40% trans). To this was added with a syringe 0.01 g (8.2 × 10⁻⁴ mole) of trifluoroacetic acid. The reaction was very exothermic, liberating a gas which was collected in the trap. Glpc analysis (15 ft 28% dimethylsulfolane on C-22 firebrick column, 40–60 mesh, at room temperature) indicated the presence of 1-butene, whose retention time was identical with that of an authentic sample and different from those of the isomeric 2-butenes.

Reaction of Cyclooct-2-en-1-yltrimethylgermanium with Trifluoroacetic Acid.—In a flask equipped with a serum cap was placed 0.716 g (3.16 × 10⁻³ mole) of cyclooct-2-en-1-yltrimethylgermanium. To this was added 0.36 g (3.16 × 10⁻³ mole) of trifluoroacetic acid with a syringe. The reaction was very exothermic and was over in less than 1 min. Water and pentane were added and the pentane layer was separated, dried, and analyzed by glpc (4 ft, 20% Carbowax 20 M on Chromosorb P column, 40–60 mesh, isothermally at 75°, flow rate 20 cc/min). The glpc indicated that all the starting material was gone and that two products were present. The products were collected (glpc); the first peak was trimethylgermanium trifluoroacetate; the second was cyclooctene. The cyclooctene had an infrared spectrum which was superimposable on that of an authentic sample. Trimethylgermanium trifluoroacetate, n^{20}D 1.3820, provided the following infrared spectral data: ν_{max} (film) 2985 (m), 2900 (m), 1750 (s), 1400 (s), 1245 (m), 1210 (s), 1170 (s), and 835 (s) cm⁻¹.

Anal. Calcd for $C_5H_9F_3GeO_2$: C, 26.02; H, 3.90; F, 24.72. Found: C, 25.81; H, 4.15; F, 24.48.

Reaction of Cyclohex-2-en-1-yltrimethylgermanium with Trifluoroacetic Acid.—To 0.2901 g (1.46 × 10⁻³ mole) of cyclohex-2-en-1-yltrimethylgermanium was added with a syringe 0.168 g (1.4 × 10⁻³ mole) of trifluoroacetic acid. An exothermic reaction commenced and was over in less than 1 min. Water and pentane were added, and the pentane layer was separated and dried over magnesium sulfate. Glpc analysis (4 ft, 20% Apiezon L on Chromosorb P column, 60–80 mesh, 100–220°, program 13°/min) indicated the presence of two peaks. The first peak was trimethylgermanium trifluoroacetate identified by infrared spectrum. The second was cyclohexene, identified by comparison of its retention time and infrared spectrum with those of an authentic sample. The starting material had completely reacted (glpc).

Reaction of Cyclopentadiene–Trimethylgermanium Hydride Adducts with Trifluoroacetic Acid.—To 0.1 g (6.7 × 10⁻⁴ mole) of cyclopentadienetrimethylgermanium hydride adducts (62.7% 5, 37.3% 6) was added 0.07 g (6.7 × 10⁻⁴ mole) of trifluoroacetic acid dropwise from a syringe. The reaction mixture was analyzed by glpc (20 ft × ³/₈ in. 20% silicone nitrile on Chromosorb P column, 60–80 mesh, isothermally at 135°, flow rate 200 cc/min), showing that 6 reacted preferentially with the trifluoroacetic acid. The cyclopentene which was formed had a retention time (glpc) which was identical with that of an authentic sample.

Hydrogenation of the Trimethylgermanium Hydride–Bicyclo-[2.2.1]heptadiene-2,5 Adducts.—To 0.70 g of the trimethylgermanium hydride–bicyclo[2.2.1]heptadiene-2,5 adducts (10, 11, and 12) dissolved in 5 ml of ethyl acetate was added 0.1 g of Adams catalyst. The mixture was hydrogenated at 25 psi in a Parr hydrogenator for 15 hr. The ethyl acetate was removed and the infrared spectrum indicated the absence of unsaturation. The nmr spectrum had trimethylgermanium singlets at τ 9.89 and 9.94 in the ratio 85:15, n^{25}D 1.4813; infrared spectrum showed ν_{max} 2960 (s), 1460 (m), 1250 (s), 1175 (w), 920 (w), 875 (w), and 840 (s) cm⁻¹; nmr spectrum gave (neat) τ 7.7 (m), 8.7 (m), 9.89 (1), and 9.94 (1).

Anal. Calcd for $C_{10}H_{11}Ge$: C, 56.40; H, 9.40. Found: C, 56.67; H, 9.61.

Reactions of Phosphorus Compounds. XIII. Kinetics and Mechanism of the Reaction of Triphenylphosphine with α,α-Dihaloamides

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The reaction of triphenylphosphine and α,α-dichloro-α-phenyl-N-methylacetanilide is a second-order polar reaction which is strongly accelerated by electron-withdrawing substituents attached to the α-phenyl group ($\rho = +2.6$). The results are consistent with a proposed mechanism involving initial attack of phosphorus on chlorine, and appear to rule out alternative mechanisms involving initial attack of phosphorus at the carbonyl oxygen, carbonyl carbon, or α carbon.

The reaction of trialkyl phosphites and trialkyl- or triarylphosphines with trichloroacetamides was shown to yield trichlorovinylamines.[1] The over-all transformation entailed the oxidation of a triply connected phosphorus compound with concomitant migration of a chlorine atom.

$$R_3P + R'CCl_2CNR''_2 \longrightarrow R_3PO + R'CCl{=}C\underset{NR_2''}{\overset{Cl}{\diagup}} \quad (1)$$
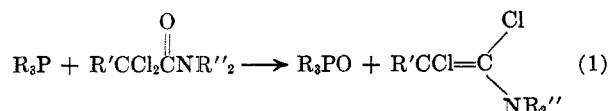
R = alkoxyl, alkyl, aryl
R' = H, Cl, F, aryl
R'' = alkyl or aryl

With the data available at that time on this and the Perkow reactions,[2] a rational mechanistic explanation

which depicted these reactions to proceed *via* attack of phosphorus on the carbonyl oxygen atom of the amide rather than the carbonyl carbon or α-carbon atom was postulated.

In order to elucidate the point of attack of the phosphine on the amide, the reaction of tertiary phosphines with α-substituted dichloroacetamides was studied. N,N-Diethyl-α,α-dichloro-α-fluoroacetamide with tributylphosphine gave a very low yield of α,β-dichloro-β-fluorovinylamine (13% at 125–130°), whereas N,N-diethyltrichloroacetamide in the same reaction gave a 74% yield of the trichloroenamine at room temperature. This striking difference in reactivity is inconsistent with attack at either the carbonyl carbon or carbonyl oxygen atoms, but strongly favors initial attack by phosphorus on the α-chlorine atom.[3] The reaction of

(1) A. J. Speziale and R. C. Freeman, *J. Am. Chem. Soc.*, **82**, 903 (1960).
(2) W. Perkow, *Chem. Ber.*, **87**, 755 (1954); W. Perkow, E. W. Krockow, and K. Knoevenagel, *ibid.*, **88**, 662 (1955).
(3) A. J. Speziale and L. R. Smith, *J. Am. Chem. Soc.*, **84**, 1868 (1962).