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Preliminary communication

STEREOCHEMISTRY OF DIMETHYLGERMYLENE ADDITION TO *E,E*- AND *E,Z*-2,4-HEXADIENES IN THE GAS PHASE

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Summary

1,1,2,5-Tetramethyl-1-germacyclopent-3-enes are formed stereospecifically in the gas-phase addition of dimethylgermylene $GeMe_2$ to *E,E*- and *E,Z*-2,4-hexadiene, the *E,E*-diene yielding 98% of *syn* product and the *E,Z*-diene yielding 96% of the *anti* isomer.

Mechanistic study of the reactions of divalent germanium species, germylenes, lags far behind the extensive work on the corresponding silicon compounds [1], and in the gas phase only the simplest germylene GeH_2 has been examined [2].

We have recently developed a convenient precursor, pentamethyldigermane, for the generation of dimethylgermylene by pyrolysis, and found in solution that it undergoes unimolecular decomposition. The resulting germylene inserts efficiently into the Ge—H bond of a parent molecule [3].

$$Me_3GeGeMe_2H \xrightarrow{250^\circ C} Me_3GeH + GeMe_2$$

$$GeMe_2 + Me_3GeGeMe_2H \rightarrow Me_3GeGeMe_2GeMe_2H$$

Pentamethyldigermane is also a clean source of dimethylgermylene in the gas phase. Vacuum flow pyrolysis employing a 540°C/10 mm by 18 cm hot zone at 1/2 Torr pressure and residence time ca. 1/10 s leads to ca. 60% decomposition. With no added substrates the products are trimethylgermane and heptamethyltrigermane in addition to recovered precursor. The absence of geminate radical recombination products tetramethyl- and hexamethyl-digermane suggests that pentamethyldigermane undergoes unimolecular decomposition in the gas phase as well as in solution.

The addition of dimethylgermylene to 1,3-dienes has now been examined. Ring et al. did not obtain 1-germacyclopent-3-ene from GeH_2 and 1,3-butadi-

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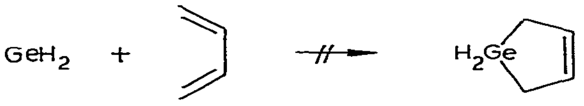
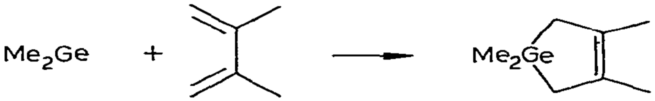
ene in the gas phase [4], but several reports have appeared of the addition of dimethylgermylene to 2,3-dimethylbutadiene in solution, employing photochemical [5] and thermal [6] methods.





Other germacyclopentenes have been obtained in the liquid phase from organometallic and photochemical reactions believed to involve germylene intermediates, but whose mechanisms remain to be fully elucidated [7].

We have obtained 1,1-dimethyl-1-germacyclopent-3-enes from the gas phase pyrolysis of pentamethyldigermane in mixtures containing a 30- to 40-fold excess of a 1,3-diene. Yields have been found to depend strongly on pressure, residence time and the composition of the reaction mixture, and have not been optimized. A 47% yield of 1,1,3,4-tetramethyl-1-germacyclopent-3-ene has, however, been obtained from 2,3-dimethyl-1,3-butadiene. The product was identified by comparison of its NMR and IR spectra, as well as its vapor chromatographic retention times, with those of an authentic sample [8]. Addition of dimethylgermylene to unsubstituted butadiene gave a 31% yield of 1,1-dimethyl-1-germacyclopent-3-ene.

When a substituent is present at the terminus of the 1,3-diene system, yields of addition products decrease, but do not disappear. A 29% yield of 1,1,2-trimethyl-1-germacyclopent-3-ene is obtained from *trans*-piperylene. This encouraged us to study the stereochemistry of addition of $GeMe_2$ to *E,E*- and *E,Z*-2,4-hexadiene. The yields of addition products from these substrates were even lower, 3.5 and 0.8% respectively, but, as the NMR spectra (Table 1) indicate, addition to both isomers of 2,4-hexadiene is highly stereoselective.

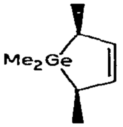
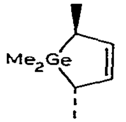
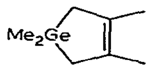
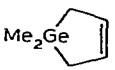
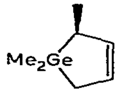
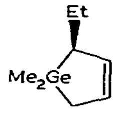
The *E,Z*-diene yields a 1,1,2,5-tetramethyl-1-germacyclopent-3-ene whose germanium-bound methyl groups are represented by a single peak in the 60 MHz ^1H NMR spectrum, while the *E,E*-diene gives an addition product with a very similar NMR spectrum in which there appear two different germanium-methyls, separated by δ 0.11. It is therefore concluded that the latter is the *syn* and the former is the *anti* isomer.

High resolution 360 MHz ^1H NMR spectroscopy allowed the quantitative assessment of the stereoselectivity of addition. The product of addition to the *E,E*-diene consisted of 98% *syn* and 2% *anti* isomers. The recovered diene substrate, initially of greater than 99% purity, was found to contain 2% of a mixture of *E,Z*-2,4-hexadiene, *E*-, and *Z*-1,3-hexadiene. Thus the addition of dimethylgermylene to *E,E*-2,4-hexadiene is greater than 98% stereospecific.

The 1,1,2,5-tetramethyl-1-germacyclopent-3-ene formed from addition of dimethylgermylene to *E,Z*-2,4-hexadiene consists of 85% *anti* and 15% *syn* isomers. The degree of stereoselectivity is however higher. Under the reaction

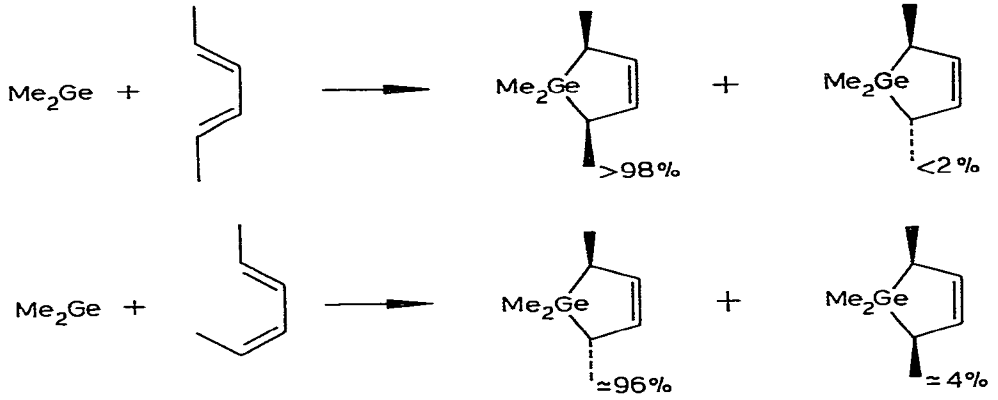
TABLE 1

^{1}H NMR SPECTRA OF 1-GERMACYCLOPENT-3-ENES FROM THE ADDITION OF DIMETHYLGERMYLENE TO 1,3-BUTADIENES

Compound	Solvent	δ (ppm)
	C_6D_6	0.16 (s, 3H, Ge—CH_3), 0.27 (s, 3H, Ge—CH_3), 1.13 (d, 6H, J 7 Hz, CH_3), 1.85 (q, 2H, J 7 Hz, CH), 5.81 (s, 2H, CH)
	C_6D_6	0.24 (s, 6H, Ge—CH_3), 1.17 (d, 6H, J 7.5 Hz, CH_3), 1.95 (q, 2H, J 7.5 Hz, CH), 5.85 (s, 2H, CH)
	C_6D_6	0.30 (s, 6H, Ge—CH_3), 1.60 (s, 4H, CH_2), 1.78 (s, 6H, CH_3)
	$CDCl_3$	0.32 (s, 6H, Ge—CH_3), 1.44 (s, 4H, CH_2), 5.92 (s, 2H, CH)
	C_6D_6	0.22 (s, 3H, Ge—CH_3), 0.27 (s, 3H, Ge—CH_3), 1.14 (d, 3H, J 7.5 Hz, CH_3), 1.53 (m, 2H, CH_2), 1.85 (m, 1H, CH), 5.92 (m, 2H, CH)
	C_6D_6	0.25 (s, 3H, Ge—CH_3), 0.32 (s, 3H, Ge—CH_3), 0.97 (t, 3H, J 7.4 Hz, CH_3), 1.58 (m, 4H, CH_2), 1.80 (m, 1H, CH), 5.95 (m, 2H, CH)

conditions the *E,Z*-2,4-hexadiene, initially 99% pure, undergoes partial rearrangement to a mixture of 85% *E,Z*- and 3% *E,E*-2,4-hexadiene plus 12% of a mixture of *E*- and *Z*-1,3-hexadiene. It has been established that *E,E*-2,4-hexadiene is 3.8 times as reactive as its *E,Z*-isomer toward $GeMe_2$ [9]. Thus the estimated degree of stereoselectivity in the addition to the *E,Z*-isomer is 96%. The adduct to the 1,3-hexadienes, 2-ethyl-1,1-dimethyl-1-germacyclopent-3-ene is also formed, in 0.6% yield. No other volatile products were found.

The observation that dichlorogermylene $GeCl_2$ undergoes addition to 2- and 2,3-disubstituted butadienes to yield 1-germacyclopent-3-enes, but no cyclic product is obtained from $GeCl_2$ and 1,3-dienes with terminal substituents, has been used to argue for concerted 1,4-addition as the reaction mechanism [10,11]. That argument can now be discounted, but the stereospecific addition observed in the present experiments is consistent with, although it does not require, concerted addition. Other mechanisms can give products with a high degree of stereoselectivity, e.g. a two-step mechanism with an allylic biradical intermediate whose ring closure is more rapid than rotation about the carbon—carbon σ bond. We are continuing our study of germylene reactions and their mechanisms.



The reactions of germylenes with carbon—carbon π systems may differ from those of their close structural analogs the silylenes [1]. The addition of SiH_2 to *E,E*- and *E,Z*-2,4-hexadienes occurs with a lower degree of stereoselectivity than that reported here for $GeMe_2$ [1,12,13]. Dimethylsilylene $SiMe_2$ undergoes addition to *E,E*-2,4-hexadiene, but the stereoselectivity was not determined [13]. Jones and Kumada have shown that $SiMe_2$ undergoes stereospecific 1,2-addition to *E*- and *Z*-2-butene [14,15].

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References

1 P.P. Gaspar in M. Jones, Jr. and R.A. Moss (Eds.), Reactive Intermediates, Vol. 1, Wiley-Interscience, New York, 1978, chapter 7, p. 229.
2 M.D. Sefcik and M.A. Ring, J. Organometal. Chem., 59 (1973) 167.
3 E.C.-L. Ma, D.P. Paquin and P.P. Gaspar, J. Chem. Soc. Chem. Commun., (1980) 381.
4 R.L. Jenkins, R.A. Kedrowski, L.E. Elliott, D.C. Tappen, D.C. Schlyer and M.A. Ring, J. Organometal. Chem., 86 (1975) 347.
5 M. Ishikawa and M. Kumada, Revs. on Si, Ge, Sn, and Pb Compounds, IV, (1979) 7.
6 W.P. Neumann and M. Schriewer, Tetrahedron Lett., (1980) 3273.
7 J. Satge, M. Massol and P. Riviere, J. Organometal. Chem., 56 (1973) 1.
8 P. Mazerolles and G. Manuel, Bull. Soc. Chim. France, (1966) 327.
9 By separate competition experiments in which $GeMe_2$ was allowed to react with a binary mixture of *trans*-piperylene and *E,E*- or *E,Z*-2,4-hexadiene, respectively.
10 S.P. Kolesnikov, A.I. Ioffe and O.M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., (1975) 978.
11 O.M. Nefedov, S.P. Kolesnikov and A.I. Ioffe, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 619.
12 P.P. Gaspar and R.-J. Hwang, J. Am. Chem. Soc., 96 (1974) 6198 reported a 1/1 ratio of *syn*- and *anti*-2,5-dimethyl-1-silacyclopent-3-ene products from both *E,E*- and *E,Z*-2,4-hexadiene. These ratios were revised to *syn/anti* 6 and 2 for the *E,E*- and *E,Z*-dienes, respectively. See ref. 1, footnote 85.
13 R.-J. Hwang, doctoral dissertation, Washington University, December, 1976.
14 V.J. Tortorelli and M. Jones, Jr., J. Am. Chem. Soc., 102 (1980) 1425.
15 M. Ishikawa, K.I. Nakagawa and M. Kumada, J. Organometal. Chem., 178 (1979) 105.