Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

ORGANOPOLYGERMANES
II*. ETHANOLYSIS OF VINYL AND PHENYL DERIVATIVES OF DISILANE AND DIGERMANE CATALYZED BY PALLADIUM(II) COMPLEXES

KEIJI YAMAMOTO AND MAKOTO KUMADA
Department of Synthetic Chemistry, Kyoto University, Kyoto (Japan)

(Received August 3rd, 1971)

SUMMARY

Vinylpentamethyldigermane (III) undergoes cleavage of the germanium–germanium bond by ethanol in the presence of palladium(II) chloride as catalyst at room temperature to give products analogous to those from the similar catalytic cleavage of vinylpentamethyldisilane (I) at 0°. In separate ethanolysis experiments, (I) is more reactive than (III), whereas the reverse is true in a competition experiment. Phenylpentamethyldisilane (VII) undergoes ethanolysis catalyzed by *trans*-[$PdCl_2(PEt_3)_2$] at 90° much more readily than the germanium analog (IX) in separate experiments, but the ethanolysis of (VII) is suppressed almost completely in the presence of (IX). A possible mechanism is discussed.

INTRODUCTION

In a previous paper[1], we reported the reaction of certain alkenyl derivatives of disilane and trisilane with ethanol under catalysis by some noble metal salts. For instance, the Si–Si bond of vinylpentamethyldisilane (I) readily undergoes cleavage even at 0° in the presence of palladium(II) chloride to give four major products [eqn. (1)].

$$\underset{\text{(I)}}{Me_3SiSiMe_2CH{=}CH_2} \xrightarrow[PdCl_2]{EtOH} Me_3SiOEt + CH_2{=}CHSiMe_2(OEt)\ \text{(II)} + EtOSiMe_2Et + Me_5Si_2Et \quad (1)$$

The results were discussed in terms of a mechanism involving initial formation of an olefin–metal π-complex followed by nucleophilic attack by ethanol on the α-silicon atom (with respect to the vinyl group complexed with the metal), leading to formation of ethoxydimethylvinylsilane (II) and trimethylsilane. The latter immediately undergoes ethanolysis catalyzed by palladium, with liberation of hydrogen, which in turn adds efficiently to the carbon–carbon double bonds present in the reaction system to give the observed ethylsilicon compounds.

In an effort to provide further insight into the mechanism of such palladium(II)

---

* For Part I see ref. 8.

complex-catalyzed ethanolysis, we have examined a similar reaction with vinylpentamethyldigermane (III) and with phenyl derivatives of disilane and digermane.

RESULTS

Reaction of vinylpentamethyldigermane (III) with ethanol

In contrast to the silicon analog (I), vinylpentamethyldigermane (III) did not undergo appreciably palladium(II) chloride-catalyzed ethanolysis at 0°. At room temperature, however, it underwent cleavage of its germanium–germanium bond to give four major products [eqn. (2)], analogous to those shown in eqn. (1). They were identified by comparison of their retention times on GLC and IR and NMR spectra with those of authentic samples.

$$\underset{\text{(III)}}{Me_3GeGeMe_2CH{=}CH_2} \xrightarrow[PdCl_2]{EtOH} Me_3GeOEt + CH_2{=}CHGeMe_2(OEt)\ \text{(IV)} + \underset{\text{(V)}}{EtOGeMe_2Et} + \underset{\text{(VI)}}{Me_5Ge_2Et} \qquad (2)$$

The extent of the reaction was monitored by GLC and an observed product distribution *vs.* time is shown in Fig. 1. When an equimolar amount of ethanol was used, 50% cleavage of the vinyldigermane (III) at room temperature required about 90 min, whereas the cleavage of the silicon analog (I) was half complete at 0° after only about 4 min (ref. 1). In short, the ethanolysis of the vinyldigermane (III) is similar but much slower than that of the vinyldisilane (I).

Interestingly, however, it was found that when an equimolar mixture of (I) and (III) was treated with two equivalents of ethanol in the presence of palladium(II) chloride at room temperature, (III) reacted faster than (I). The degrees of conversion of the two reactants at various reaction times are given in Table 1.

TABLE 1

ETHANOLYSIS OF AN EQUIMOLAR MIXTURE OF $CH_2{=}CHSi_2Me_5$ (I) AND $CH_2{=}CHGe_2Me_5$ (III) IN THE PRESENCE OF $PdCl_2$ AS CATALYST

Compound	Conversion (%) after a reaction time (min) of				
	0	10	35	85	1000
$Me_5Si_2CH{=}CH_2$ (I)	0	10	17	20	25
$Me_5Ge_2CH{=}CH_2$ (III)	0	12	25	39	66

Reaction of phenylpentamethyldisilane (VII) with ethanol

We briefly reported previously that phenylpentamethyldisilane (VII) also undergoes cleavage of the silicon–silicon bond with evolution of hydrogen, upon treatment with ethanol in the presence of palladium(II) chloride to give two compounds, neither of which is a hydrogenated product.

$$\underset{\text{(VII)}}{PhMe_2SiSiMe_3} \xrightarrow[PdCl_2]{EtOH} \underset{\text{(VIII)}}{PhMe_2SiOEt} + EtOSiMe_3 + H_2 \qquad (3)$$

The same reaction can be effected under *homogeneous conditions* in a degassed sealed glass ampule using *trans*-[$PdCl_2(PEt_3)_2$] as catalyst. After 26 h heating at 90°, the reaction depicted by eqn. (3) was 65% complete (by GLC analysis). Throughout the reaction, the mixture was clear and homogeneous, but on exposure to the air it gradually turned grey and formed a palladium mirror on the walls.

Attempted reaction of phenylpentamethyldigermane (IX) with ethanol

Here again, in contrast to the silicon analog (VII), phenylpentamethyldigermane (IX) displayed a very low reactivity to ethanolysis catalyzed by *trans*-[$PdCl_2(PEt_3)_2$], and 95% of the starting substance was recovered unchanged from the attempted reaction under similar conditions. In addition, the presence of the phenyldigermane (IX) was found to suppress the ethanolysis of the phenyldisilane (VII) completely when an equimolar mixture of these two was used.

DISCUSSION

The results obtained for the palladium-catalyzed ethanolysis of the element–element bond of vinyl and phenyl derivatives of disilane and digermane are summarized as follows. For the ethanolysis to proceed, a catalytic amount of a palladium(II) compound is sufficient, and the reaction appears not to be inhibited by a cleavage product such as $CH_2{=}CHSiMe_2(OEt)$ (II). In separate ethanolysis experiments, the vinyldisilane (I) is more reactive than the germanium analog (III), whereas the reverse is true in a competition experiment. Also, in separate experiments the phenyldisilane (VII) is much more reactive than the phenyldigermane (IX), the latter being practically inert, whilst in a competition experiment the former, too, remains unchanged.

The similar difference in reactivity order obtained in separate experiments from that in competition experiments has been recognized for catalytic hydrogenation of olefins over platinum black and for catalytic addition of various silicon hydrides to 1,1,2-trifluoro-2-chloroethylallyl ether in the presence of Pt/C, and can be attributed to the fact that a less reactive olefin can, by being more strongly complexed or absorbed, exclude a more reactive olefin from the catalyst surface[2].

Our results may be best explained similarly by assuming that (*i*) the vinyl and phenyl derivatives of digermane are more strongly complexed to the palladium catalyst than those of disilane, and (*ii*) nucleophilic attack of solvent ethanol on the silicon is faster than on the germanium atom. The assumption (*i*) suggests that, in the initial olefin–palladium π-complex formation, the electron donation from olefin to metal is more important than the back-donation from a filled metal *d* orbital to the olefin π^* orbital, since the inductive electron-donating effect will be expected to be stronger for pentamethyldigermanyl group than for pentamethyldisilanyl group. A reasonable assumption on the same basis that vinylpentamethyldisilane (I) and -digermane (III) interact with the catalyst more strongly than ethoxydimethylvinylsilane (II) and -germane (IV), respectively, can account for the reason why only a catalytic amount of a palladium(II) compound is enough to cause complete cleavage of the element–element bond, if a sufficient amount of ethanol is employed. The assumption (*ii*) seems reasonable in view of the fact that this reactivity sequence is generally found for nucleophilic substitution at the metal atom, though the reasons for these relative reactivities are not fully understood[3].

EXPERIMENTAL

Materials

The compounds listed below are known and were prepared by standard methods: Me_3GeOEt[4], $Me_2Ge(OEt)_2$[5], $PhMe_2SiOEt$ (VIII)[6], and *trans*-$[PdCl_2(PEt_3)_2]$[7]. Several new compounds were prepared as follows.

Vinylpentamethyldigermane (III)

To a solution of vinylmagnesium chloride, prepared from 1.20 g (0.05 g-atom) of magnesium turnings and dry vinyl chloride in anhydrous tetrahydrofuran (THF), was added 7.0 g (0.027 mole) of chloropentamethyldigermane (see below). The mixture was heated to reflux for 3 h, and hydrolyzed with dilute hydrochloric acid. The organic layer was washed until neutral and fractionally distilled to give 4.0 g (60% yield) of (III), b.p. 153°, n_D^{20} 1.4875. (Found: C, 33.89; H, 7.40. $C_7H_{18}Ge_2$ calcd.: C, 33.98; H, 7.33%.) The NMR spectrum (15% in $CDCl_3$) displayed peaks at δ 0.25 ($GeMe_3$), 0.30 ($GeMe_2$), and 5.36–4.70 ppm (vinyl protons).

Ethoxydimethylvinylgermane (IV)

To a heated solution of 20.0 g (0.104 mole) of dimethyldiethoxygermane[5] in dry THF (60 ml) was added dropwise a THF solution of vinylmagnesium chloride (1.2 *M*, 100 ml). The mixture was refluxed for an additional 1 h, and the solvent was then removed by distillation through a 30 cm Vigreux column. The residue was extracted with dry pentane. The extract was fractionally distilled to give 7.0 g (40% yield) of (IV), b.p. 122°, n_D^{20} 1.4310. (Found: C, 40.73; H, 7.99. $C_6H_{14}GeO$ calcd.: C, 41.24; H, 8.07%.) NMR (20% in CCl_4): δ 0.38 ($GeMe_2$), 1.10 ($O{-}C{-}CH_3$, t, *J* 7.0 Hz), 3.55 ($O{-}CH_2{-}C$, q, *J* 7.0 Hz) and 5.46–4.59 ppm (vinyl protons).

Ethylpentamethyldigermane (VI)

As described in the preparation of (III), 4.0 g (0.016 mole) of chloropentamethyldigermane was treated with an excess of ethylmagnesium bromide in ether (ca. 1 *M*, 40 ml). The mixture was worked up in the usual way. Fractional distillation gave 2.5 g (64% yield) of (VI), b.p. 156–158°, n_D^{20} 1.4703. (Found: C, 33.99; H, 8.09. $C_7H_{20}Ge_2$ calcd.: C, 33.71; H, 8.08%.) NMR (15% in CCl_4): δ 0.17 ($GeMe_2$), 0.22 ($GeMe_3$) and 1.25–0.60 ppm (Et).

Phenylpentamethyldigermane (IX)

Phenyldimethylgermyllithium was prepared from 4.1 g (0.58 g-atom) of lithium and 31.0 g (0.14 mole) of phenyldimethylchlorogermane in 150 ml of THF[8]. Unchanged lithium was removed by filtration and the filtrate was added dropwise to 22.0 g (0.14 mole) of trimethylchlorogermane dissolved in 30 ml of THF over 0.5 h. The mixture, after an additional 10 min stirring, was hydrolyzed with dilute hydrochloric acid. The organic layer was worked up in the usual way and finally fractionally distilled to give 33.0 g (77% yield) of (IX), b.p. 69–70°/2 mm, n_D^{20} 1.5321. (Found: C, 44.38; H, 6.69. $C_{11}H_{20}Ge_2$ calcd.: C, 44.40; H, 6.79%.) NMR (15% in CCl_4): δ 0.30 ($GeMe_3$), 0.51 ($GeMe_2$), and 7.30–6.90 ppm (phenyl protons).

Chloropentamethyldigermane[9]

In essentially the same manner as that used for chlorodephenylation of diphenyldimethylgermane[8], a mixture of 18.5 g (0.062 mole) of phenylpentamethyldigermane (IX), 0.15 g of anhydrous aluminum chloride and 50 ml of chloroform was treated with excess dry hydrogen chloride at room temperature for 0.5 h. At this point (GLC monitoring having revealed that the reaction was complete) a small amount of acetone was added to the mixture to deactivate the catalyst, and then the solvent and benzene formed from reaction were removed by distillation. The residue was distilled under reduced pressure to give 15.0 g (98 % yield) of chloropentamethyldigermane, b.p. 64–65°/15 mm (166–167°/760 mm), n_D^{20} 1.4926. (Found: C, 23.76; H, 5.82. $C_5H_{15}ClGe_2$ calcd.: C, 23.48; H, 5.91 %.) NMR (15% in CCl_4): δ 0.45 ($GeMe_3$) and 0.76 ppm ($GeMe_2$).

$PdCl_2$- catalyzed ethanolysis of (III)

(*a*). In a 50 ml Erlenmeyer flask, previously flushed with pure nitrogen and sealed with a serum cap, was placed a mixture of 0.990 g (4.0 mmole) of (III), 0.188 g (4.0 mmole) of ethanol, 35.5 mg (5 mole-%) of $PdCl_2$ and 0.537 g (4.0 mmole) of *p*-cymene (as an internal standard for GLC analysis) , and stirred magnetically at room temperature. Palladium (II) chloride was gradually reduced to black precipitates and slow cleavage of the germanium–germanium bond was observed by monitoring the progress of reaction by GLC (DOP 2.5 m, at 125°) of the organic layer. When a five-fold excess of ethanol was used, much faster cleavage was observed to occur (see Fig. 1). Two of the principal products, Me_3GeOEt and $Me_2Ge(OEt)CH{=}CH_2$(IV), were isolated pure by preparative GLC and identified by comparison of their NMR and IR spectra with those of the authentic samples. Although the other two principal products, $Me_2EtGeOEt$ (V) and $EtGe_2Me_5$(VI) could not be separated completely pure because of the proximity of their positions on GLC to those of (IV) and (III), respectively, they were identified by comparison of the retention times on GLC and NMR spectra of the samples in a slightly impure state with those of the authentic samples.

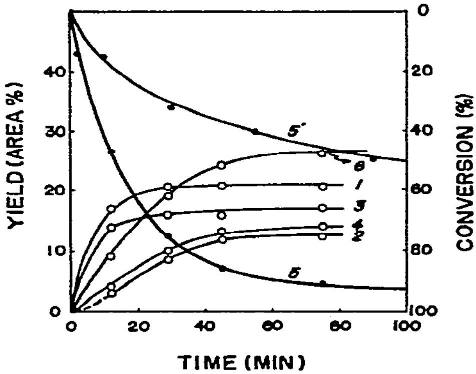

Fig. 1. Reaction of vinylpentamethyldigermane (III) with a five-fold excess of ethanol in the presence of 5 mole-% of palladium(II) chloride at room temperature. 1, Me_3GeOEt; 2, $(Me_3Ge)_2O$; 3, $EtOMe_2GeCH{=}CH_2$(IV); 4, $EtOMe_2GeEt$ (V); 5, Conversion of (III); 6, Me_5Ge_2Et(VI). 5', Conversion of (III) when taken with an equimolar amount of ethanol.

(*b*). A mixture of 0.405 g (2.56 mmole) of CH_2=$CHSi_2Me_5$ (I), 0.627 g (2.54 mmole) of CH_2=$CHGe_2Me_5$ (III), 0.231 g (5.02 mmole) of ethanol and 0.344 g (2.56 mmole) of *p*-cymene (an internal standard for GLC) was similarly treated with $PdCl_2$ (18 mg, 0.1 mmole; 2 mole-%) at room temperature. The conversion of the two reactants at various times is given in Table 1.

trans-$[PdCl_2(PEt_3)_2]$ *catalyzed ethanolysis of phenylpentamethyldisilane* (*VII*)

A mixture of 0.60 g (3.0 mmole) of $PhSi_2Me_5$ (VII), 0.50 g (11 mmole) of ethanol and 4.0 mg (1×10^{-2} mmole) of *trans*-$[PdCl_2(PEt_3)_2]$ was heated at 90° for 26 h in a degassed sealed glass ampoule. At this point, an aliquot (1/10) of the clear reaction mixture was taken and 25.5 mg (0.13 mmole) of n-tetradecane (an internal standard for GLC) was added to it. GLC analysis indicated that there were 0.195 mmole of $Me_2PhSiOEt$ (VIII) and 0.105 mmole of unchanged (VII).

Attempted ethanolysis of phenylpentamethyldigermane (*IX*) *and of a mixture of phenylpentamethyldisilane* (*VII*) *and -digermane* (*IX*)

(*a*). A mixture of 0.90 g (3.0 mmole) of $PhGe_2Me_5$ (IX), 0.5 g (11 mmole) of ethanol and 4.0 mg (1×10^{-2} mmole) of *trans*-$[PdCl_2(PEt_3)_2]$ was heated under the same conditions as above. A trace of Me_3GeOEt and 95% of (IX) remaining unchanged were detected by GLC.

(*b*). A mixture of 0.26 g (1.2 mmole) of $PhSi_2Me_5$ (VII), 0.37 g (1.2 mmole) of $PhGe_2Me_5$ (IX), and 0.4 g (9 mmole) of ethanol was similarly treated with *trans*-$[PdCl_2(PEt_3)_2]$ (4 mg) at 90° for 26 h. None of the reaction products except a trace of Me_3GeOEt was detected by GLC of the mixture, (VII) and (IX) being recovered unchanged.

ACKNOWLEDGEMENTS

The cost of this research was defrayed in part from the Grant-in-aid for scientific research of the Ministry of Education, to which the authors' thanks are due. The authors are also grateful to Tokyo-Shibaura Electric Co., Ltd. and Nitto Electric Industrial Co., Ltd for support of this work.

REFERENCES

1 K. Yamamoto, M. Kumada, I. Nakajima, K. Maeda and N. Imaki, *J. Organometal. Chem.*, 13 (1968) 329.
2 For a review, see C. Eaborn and R. W. Bott, in A. G. MacDiarmid (Ed), *Organometallic Compounds of the Group IV Elements*, Vol. 1, Part 1, Marcel Dekker, New York, 1968, p. 256.
3 (a) R. W. Bott, C. Eaborn and T. W. Swaddle, *J. Chem. Soc.*, (1963) 2342.
(b) G. Schott and C. Harzdorf, *Z. Anorg. Chem.*, 307 (1960) 105.
(c) D. G. Anderson and D. E. Webster, *J. Chem. Soc. B*, (1968) 765.
4 E. W. Abel, D. A. Armitage and D. B. Brady, *J. Organometal Chem.*, 5 (1966) 130.
5 G. Ya Zueva, I. F. Manucharova, J. P. Yakovlev and V. A. Ponomarenko, *Izv. Akad. Nauk S.S.S.R. Neorgan. Mater.*, 2 (1960) 229; *Chem. Abstr.*, 64 (1966) 17631e.
6 H. Freiser, M. V. Eagle and J. L. Speier, *J. Amer. Chem. Soc.*, 75 (1953) 2824.
7 *Inorg. Synth.*, 11 (1968) 108; *cf.* F. G. Mann and D. Purdie, *J. Chem. Soc.*, (1935) 1549.
8 M. Kumada, S. Sakamoto and M. Ishikawa, *J. Organometal. Chem.*, 17 (1969) 235.
9 E. J. Bulten and J. G. Noltes, *J. Organometal. Chem.*, 15 (1968) P18.