

Stereospecific Route to Asymmetric Vinylgermanes: Hydrogermylation of Phenylacetylene Catalysed by Rhodium and Platinum Complexes

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Summary The stereochemistry of homogeneous catalysed hydrogermylation has been studied; phenylacetylene leads to three adducts and addition occurs with retention of configuration at the germanium atom.

ATTEMPTS to synthesize optically active vinylgermanes led us to study the hydrogermylation of phenylacetylene. In the absence of catalyst, the addition occurs when the reactants are heated to *ca.* 100 °C, but low yields are often obtained.¹ We report that chlorotris(triphenylphosphine)-rhodium(I), which activates hydrosilylation,² and *cis*-dichloro-bis(triphenylphosphine)platinum(II) are effective catalysts for hydrogermylation in 1% concentration.

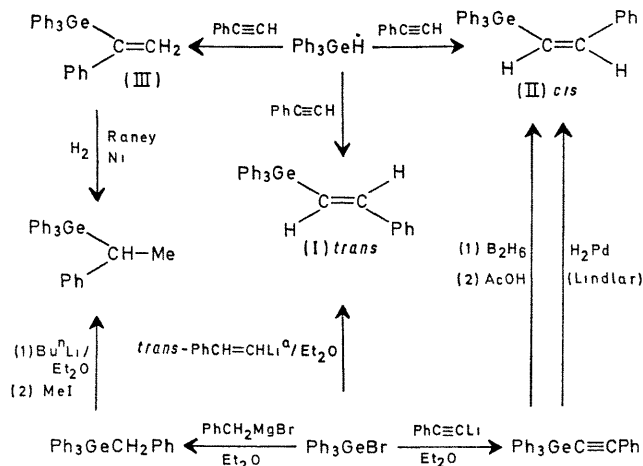
The adduct (III) has been reported once before, in the addition to prop-2-ynyl chloride.⁴ (III) is formed mainly when platinum is used as catalyst, while rhodium predominantly gives *cis*-addition.

The stereochemistry of the hydrogermylation has been studied by addition of asymmetric organogermanes: α -naphthylphenylmethylgermane,⁵ α -NpPhMeGe*H, $[\alpha]_D + 25.0^\circ$, α -naphthylphenylisopropylgermane,⁶ α -NpPhPrⁱ-Ge*H, $[\alpha]_D + 1.6^\circ$. Addition of these models affords an oily mixture of the three adducts. Fractional crystallization from methanol gives pure *trans*-adduct. Results are given in Table 2.

Assuming that chlorination proceeds with retention of

TABLE 1

R ₃ GeH	Catalyst	Reaction temperature (°C)	Reaction time (h)	Total yield (%)	(I) (%)	(II) (%)	(III) (%)
Ph ₃ GeH	(PPh ₃) ₃ RhCl	20	3	85	82	15.5	2.5
Ph ₃ GeH	<i>cis</i> -(PPh ₃) ₂ PtCl ₂	50	10	70	85	10	5
Ph ₃ GeH	H ₂ PtCl ₆ ·6H ₂ O	20	0.5	78	70	0.5	29.5
Ph ₃ GeH	None	50	96	38			
α -NpPhMeGeH	(PPh ₃) ₃ RhCl	20	2.5	82	89	8	3
α -NpPhMeGeH	<i>cis</i> -(PPh ₃) ₂ PtCl ₂	50	10	71	84	9	7
α -NpPhMeGeH	H ₂ PtCl ₆ ·6H ₂ O	20	0.5	68	71	2	27
α -NpPhMeGeH	None	50	150	12			
α -NpPhPr ⁱ GeH	(PPh ₃) ₃ RhCl	20	24	70		24	6
α -NpPhPr ⁱ GeH	<i>cis</i> -(PPh ₃) ₂ PtCl ₂	50	48	51	53	28	19
α -NpPhPr ⁱ GeH	H ₂ PtCl ₆ ·6H ₂ O	20	4	59	69	<i>ca.</i> 0	31

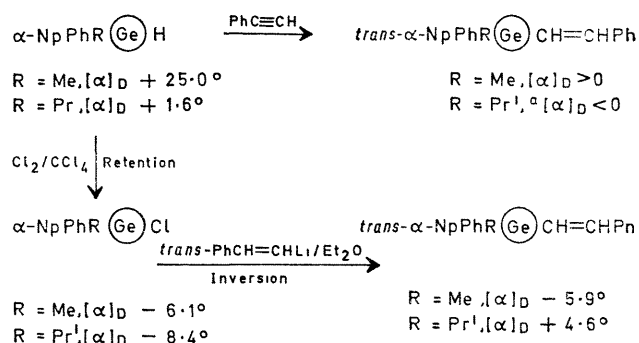


* *trans*- β -Styryl-lithium was prepared according to the method of D. Seyferth *et al.* (ref. 3).

Coupling reactions between triphenylgermane and phenylacetylene result in the formation of three identified adducts (I), (II), (III) (Scheme 1). (I) results from *cis*-addition, (II) from *trans*-addition, and (III) from a Markovnikov addition. Results are summarized in Table 1.

configuration at the germanium atom,⁷ and that treatment with *trans*- β -styryl-lithium in diethyl ether occurs with inversion as for *n*-butyl-lithium and methyl-lithium,⁸ then the hydrogermylation takes place with retention of configuration (Scheme 2).

Analogous results were obtained for the addition of similar silicon compounds to oct-1-ene using homogeneous and heterogeneous platinum catalysts,⁹ as well as with diphenylacetylene in the presence of platinum on charcoal.¹⁰



* With this model, the *trans*-adduct has not been isolated from the initial mixture of isomers.

TABLE 2

R_3GeH	Catalyst	$[\alpha]_D$ of adducts (°)	$[\alpha]_D$ of <i>trans</i> -adduct (°)	Stereochemistry
α -NpPhMeGeH	(PPh ₃) ₃ RhCl	+ 6.4	+ 8.1	Retention
α -NpPhMeGeH	<i>cis</i> -(PPh ₃) ₂ PtCl ₂	+ 5.6	+ 8.1	"
α -NpPhMeGeH	H ₂ PtCl ₆ ·6H ₂ O	+ 6.8	+ 8.6	"
α -NpPhMeGeH	None	+ 5.6	+ 7.1	"
α -NpPhPr ¹ GeH	(PPh ₃) ₃ RhCl	- 5.8	- ^a	"
α -NpPhPr ¹ GeH	<i>cis</i> -(PPh ₃) ₂ PtCl ₂	- 5.0	- ^a	"
α -NpPhPr ¹ GeH	H ₂ PtCl ₆ ·6H ₂ O	- 5.6	- ^a	"

^a We did not succeed in crystallizing these oily mixtures. Analogous observations have been made with this model.⁶

The adduct obtained by hydrogermylation has a higher specific rotation than the same product obtained by a coupling reaction between *trans*- β -styryl-lithium and chlorogermane. Hydrogermylation provides a route to asymmetric vinylgermanes. The rhodium complexes have a higher selectivity than the platinum complexes.

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- ¹ M. Lesbre and J. Satge, *Compt. rend.*, 1960, **250**, 2220; M. C. Henry and M. F. Downey, *J. Org. Chem.*, 1961, **26**, 2299.
- ² R. N. Haszeldine, R. V. Parish, and D. J. Parry, *J. Chem. Soc. (A)*, 1969, 683.
- ³ D. Seylerth, L. G. Vaughan, and R. Suzuki, *J. Organometallic Chem.*, 1964, **1**, 437.
- ⁴ M. Massol, J. Satge, and M. Lesbre, *J. Organometallic Chem.*, 1969, **17**, 25.
- ⁵ A. G. Brook and G. J. D. Peddle, *J. Amer. Chem. Soc.*, 1963, **85**, 1869.
- ⁶ F. Carre and R. Corriu, *J. Organometallic Chem.*, 1970, **25**, 395.
- ⁷ A. G. Brook and G. J. D. Peddle, *J. Amer. Chem. Soc.*, 1963, **85**, 2338.
- ⁸ C. Eaborn, R. E. E. Hill, and P. Simpson, *Chem. Comm.*, 1968, 1077.
- ⁹ L. H. Sommer, J. E. Lyons, and H. Fujimoto, *J. Amer. Chem. Soc.*, 1969, **91**, 7051.
- ¹⁰ A. G. Brook, K. H. Pannell, and D. G. Anderson, *J. Amer. Chem. Soc.*, 1968, **90**, 4375.