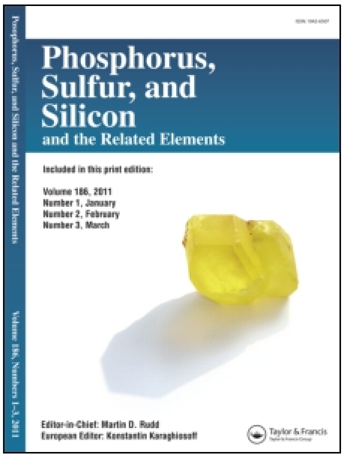
This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

LIGAND EFFECTS IN PALLADIUM(0)-CATALYZED REARRANGEMENT OF A SILICON SUBSTITUTED VINYLOXIRANE

Franck Le Bideau[a]; Max Malacria[a]
[a] Université P. et M. Curie, Laboratoire de Chimie Organique de Synthèese, associé au CNRS, Paris, Cedex 05, France

To cite this Article Bideau, Franck Le and Malacria, Max(1995) 'LIGAND EFFECTS IN PALLADIUM(0)-CATALYZED REARRANGEMENT OF A SILICON SUBSTITUTED VINYLOXIRANE', Phosphorus, Sulfur, and Silicon and the Related Elements, 107: 1, 275 — 277

To link to this Article: DOI: 10.1080/10426509508027943

URL: http://dx.doi.org/10.1080/10426509508027943

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur, and Silicon, 1995, Vol. 107, pp. 275–277
Reprints available directly from the publisher
Photocopying permitted by license only

Communication

LIGAND EFFECTS IN PALLADIUM(0)-CATALYZED REARRANGEMENT OF A SILICON SUBSTITUTED VINYLOXIRANE

FRANCK LE BIDEAU and MAX MALACRIA*
Université P. et M. Curie, Laboratoire de Chimie Organique de Synthèse, associé au CNRS, Tour 44, B.229, 4 place Jussieu, 75252 Paris Cedex 05, France

(Received May 25, 1995; in final form July 10, 1995)

Palladium(0)-catalyzed rearrangement of silylated vinyloxirane **4** is depending on ligand effects.

Key words: *tert*-butyldiphenylsilylvinylepoxide, vinyloxirane, 1,2-silicon shift, Brook rearrangement, Palladium(0), ligand effects.

We previously reported that silicon substituted vinyloxiranes of type **1** rearrange under palladium(0)-catalyzed conditions to give, depending on the size of the silyl substituents, compounds **2** or **3** (Scheme I).[1]

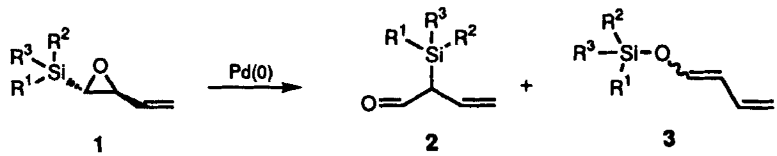
Aldehydes **2** occur from a 1,2-silicon shift while dienes **3** are the products of a Brook rearrangement.[2] In the case of *tert*-butyldiphenylsilylvinylepoxide **4**, using $P(OiPr)_3$ as ligand, we observed[3] the formation of both aldehyde **5** and diene **6** respectively in 71% and 26% yields (Scheme II). More interestingly, a total chirality transfer was observed in the isomerization of compound **4** to aldehyde **5**. The π-allyl palladium complex was formed by oxidative addition of the vinyloxirane to palladium(0) with inversion.[4] The steric interaction between the silicon and the palladium would favor the rotation around the carbon-carbon bond and furthermore the silylated group would attack *anti* to the metal (Scheme III). Obviously, determination of conditions which would allow the totally selective formation of **5** will enhance the synthetic usefulness of this stereoselective process.

In this paper, we describe the dramatic influence of the ligand on the product distribution for this reaction.

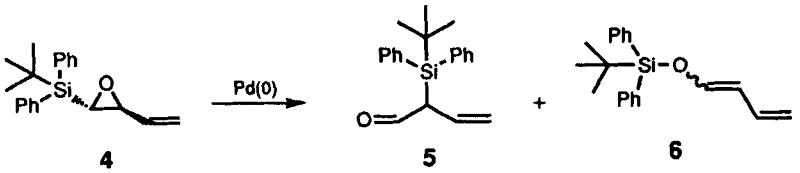
Exposure of racemic vinyloxirane **4** to a catalytic amount of zerovalent palladium species generated *in situ* from 2.6 mol % $Pd(OAc)_2$ and 16 mol % of various ligands, in THF at different temperatures and reaction times afforded the adducts **5** and **6** in good chemical yields as summarized in Table I.

The total inversion in the product distribution from TMEDA to $P(OPh)_3$ can be explained in terms of more or less aceptor properties of the ligands. It is worthy of note that with the latter, the unique product isolated was the aldehyde **5**.

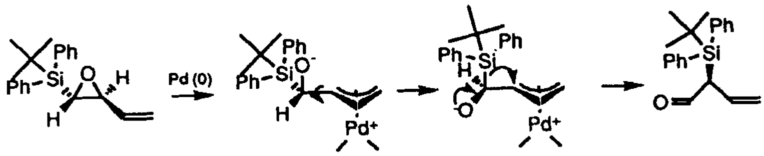
Åkermark and Vitagliano[5] showed by ^{13}C-NMR that the three carbons of (η^3-allyl) palladium systems were electronically affected by a variation of ligands (Scheme IV). The electronic distribution is responsible for the regioselectivity in the nucleophilic attack of both amines and malonates anions. Acceptor ligands like $P(OPh)_3$ induce positive charge at the more (η^3-allyl) terminus. In this case, the electronic



SCHEME I Palladium(0)-catalyzed rearrangements of silicon substituted vinyloxiranes.



SCHEME II Palladium(0)-catalyzed rearrangement of *tert*-butyldiphenylsilylvinylepoxide.



SCHEME III Mechanism of the formation of aldehyde 2.

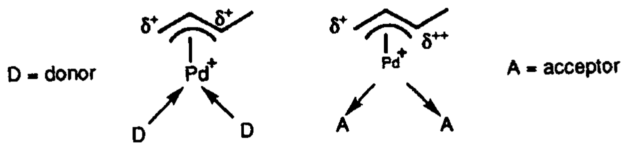
TABLE I

Rearrangement of vinyloxirane 4 under various palladium(0) conditions.

Entry	Ligand	5[a]	6[a]	Temp.(°C)	Time (h)
1	TMEDA[b]	2	78	67	12
2	dppe[b]	13	66	67	60
3	PBu_3	16	73	25	3
4	PPh_3[b]	33	39	67	12
5	$P(OEt)_3$	40	41	25	3
6	$P(OMe)_3$	51	31	25	3
7	$P(O\textit{i}Pr)_3$	71	26	25	3
8	$P(O\text{-}CH_2\text{-}C)_3\text{-}Et$	64	24	25	3
9	$P(OPh)_3$[b]	90	-	46	3

[a] isolated yields ; [b] No reaction occurs at 25°C within 2 h.

factor predominates and the nucleophilic attack will occur at this carbon. Donor ligands like TMEDA decrease the stabilizing effect of the induced positive charge given by a substituent and the steric effect in the (η^3-allyl) predominates resulting in a higher proportion of nucleophilic attack at the least substituted carbon. In our



SCHEME IV Electronic effect of donor and acceptor ligands on a π-allyl palladium unit.

case, the sole effect to consider is the growth in electropositive character induced on the proximal position of the intermediate which reinforce the 1,2 migration of the silicon 'nucleophile' to the detriment of the Brook rearrangement. Except for PPh_3 which should be more attractive than $P(OMe)_3$, our results are in good agreement with this classification. The best acceptor ligand $P(OPh)_3$ (entry 9) induces a highest degree in 1,2-silicon shift (with the same level of chirality transfert) whereas the more donor ligand TMEDA (entry 1) is found to favor the Brook rearrangement.

In summary, we showed that in addition to the effect of the substituents on the silicon, the competition between palladium(0)-catalyzed 1,2-shift and Brook rearrangement is severely dependent on the electronic effects induced by the ligands. Having thus found conditions to achieve this palladium(0)-catalyzed 1,2-silicon shift in very high chemical and optical yields, work is now under very active progress in our laboratory to illustrate the synthetic usefulness of this chiral aldehyde.

EXPERIMENTAL

To a stirred solution of $Pd(OAc)_2$ (6 mg, 0.03 mmol) and ligand (0.16 mmol) in THF (5 ml) under an argon atmosphere was added vinyloxirane **4** (308 mg, 1.00 mmol). After 2 h at room temperature (or THF reflux for entry 1, 2, 4, 9 of Table I), the solvent was evaporated and the residue was purified by flash chromatography (petroleum ether:ether/90:10) to give aldehyde **5** and diene **6** (yields are reported in Table I).

Aldehyde **5**: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.73 (1 H, d, J = 3.1 Hz), 7.7–7.3 (10 H, m), 6.13 (1 H, dt, J = 17.1, 10.1 Hz), 5.02 (1 H, d, J = 10.1 Hz), 4.88 (1 H, d, J = 17.1 Hz), 3.96 (1 H, dd, J = 10.1, 3.1 Hz), 1.16 (9 H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) 199.7, 136.3, 131.9, 131.7, 130.8, 129.8, 127.8, 117.0, 53.0, 28.2, 19.7

Diene **6**: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.9–7.7 (4 H, m), 7.6–7.4 (6 H, m), 7.12 (1 H, dt, J = 17.2, 10.6 Hz), 6.28 (1 H, d, J = 5.8 Hz), 5.33 (1 H, dd, J = 10.6, 5.8 Hz), 5.28 (1 H, d, J = 17.2 Hz), 5.09 (1 H, d, J = 10.6 Hz), 1.22 (9 H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) 140.7, 135.4, 132.4, 130.0, 129.8, 127.9, 113.6, 111.2, 26.5, 19.3; IR (neat) 3060, 3040, 2940, 2920, 2880, 2840, 1640, 1590, 1465, 1420, 1250, 1170, 1100, 1070, 1000, 820, 700

ACKNOWLEDGEMENT

F.L.B. thanks the Centre National de la Recherche Scientifique for his fellowship.

REFERENCES

1. (a) F. Gilloir and M. Malacria, *Tetrahedron Lett.*, **33**, 3859 (1992); (b) F. Le Bideau, F. Gilloir, Y. Nilsson, C. Aubert and M. Malacria, *Tetrahedron Lett.*, **36**, 1641 (1995).
2. A. G. Brook, *Acc. Chem. Res.*, **7**, 77 (1974).
3. F. Le Bideau, C. Aubert and M. Malacria, *Tetrahedron: Asymmetry*, **6**, 697 (1995).
4. T. Hayashi, T. Hagihara, M. Konishi and M. Kumada, *J. Am. Chem. Soc.*, **105**, 7767 (1983).
5. (a) B. Åkermark, B. Krakenberger, S. Hansson and A. Vitagliano, *Organometallics*, **6**, 620 (1987); (b) B. Åkermark, K. Zetterberg, S. Hansson, B. Krakenberger and A. Vitagliano, *J. Organomet. Chem.*, **335**, 133 (1987).