Pergamon

Tetrahedron Letters, Vol. 38, No. 17, pp. 3081-3084, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)00550-9

A New Class of Oxygen Nucleophiles for Regioselective 1,4-Addition to Butadiene Monoxide Catalyzed by Palladium Complexes

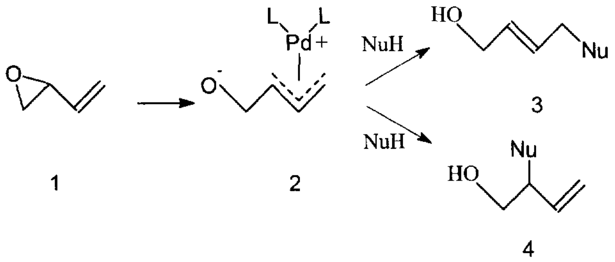
Daniele Bianchi, Cecilia Querci*, Marco Ricci and Roberto Santi

EniChem, Istituto G. Donegani, 28100 Novara, Italy

Abstract: Butadiene monoxide reacts with high regioselectively with anhydrides to give preferentially diesters of 2-buten-1,4-diol in presence of palladium phosphine complexes.
Reaction regioselectivity is strongly influenced by the nature of palladium ligand, anhydride and solvent. © 1997 Published by Elsevier Science Ltd.

Reactions of allylic epoxides with various nucleophiles catalyzed by palladium complexes via π-allyl-palladium intermediate are well known[1-6]. As shown in Scheme 1, the nucleophile NuH can attack the π-allyl-complex to give two isomeric products **3** and **4**:

Scheme 1



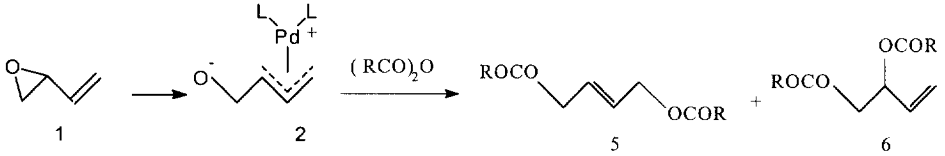
With carbon nucleophiles, the attack takes place at the terminal position to give the 1,4 isomer, while when oxygen nucleophiles are used the addiction is scarcely selective, and the 1,2 isomer is preferred.
Only triphenylsilanol reacts with vinyl epoxide[7], in presence of Pd complexes with bidentate ligands, to give the 1,4 isomer.

In this paper we report a new method for the regioselective 1,4 functionalization of butadiene monoxide **1** by using carboxylic anhydrides.

We were interested in the synthesis of 2-buten-1,4-diol from butadiene monoxide, as it is easily transformed into 1,4-butanediol, an important intermediate in the synthesis of polymers Since water is not a suitable nucleophile for the reaction with π-allyl palladium complex,[7] we moved toward different oxygen nucleophiles, such as carboxylates, which would also afford 2-buten-1,4-diol, after hydrolysis of the produced hydroxyesters. Actually carboxylic acids turned out to be good nucleophiles for this reaction but they were poorly regioselective and the 1,2 attack was preferred.

So we wondered if the selectivity could be improved by using a different way to generate the carboxylate nucleophile, *i.e.* upon reaction of complex **2** with a carboxylic anhydride.(Scheme 2). This was indeed the case and a drastic improvement of the regioselectivity of the reaction was observed.

Scheme 2



In a typical experiment the palladium complex was formed in THF starting from palladium bis(dibenzylidenacetone)[8] (0.007 mmole) and the phosphine (0.042 mmole), then the anhydride (1 mmole), a solution of butadiene monoxide (1 mmole) and an internal standard were added. The solution was vigorously stirred and after the required time was analyzed by GC.

The reaction was carried out with various palladium ligands and carboxylic anhydrides as shown in Tablel1.

Table 1. Palladium Complexes Catalyzed Reaction between Butadiene Monoxide and Carboxylic Anhydrides.

Ligand	Anhydride	Conversion %[a] butadiene monoxide	Time (h)	**5/6** (% yield)[a]	pKa[b]	ϑ[c]
Ph_2MeP	$(CH_3CO)_2O$	100	1	60/30	4.6	136
Ph_2MeP	$(C_3H_7CO)_2O$	100	0,25	73/24	"	"
Ph_2MeP	$(t\text{-}ButCO)_2O$	100	1	83/11	"	"
$PhMe_2P$	$(C_3H_7CO)_2O$	100	1	66/22	6.5	122
Ph_3P	$(CH_3CO)_2O$	23	4	9/9[d]	2.73	145
Ph_3P	$(C_3H_7CO)_2O$	56	4	20/14[d]	"	"
$(4\text{-}CH_3C_6H_4)_3P$	$(CH_3CO)_2O$	29	4	10/8[d]	3.84	145
$(4\text{-}CH_3C_6H_4)_3P$	$(C_3H_7CO)_2O$	57	4	18/12[d]	"	"
$(4\text{-}ClC_6H_4)_3P$	$(CH_3CO)_2O$	33	4	18/13[d]	1.03	145
$(4\text{-}ClC_6H_4)_3P$	$(C_3H_7CO)_2O$	100	4	34/26[d]	"	"
$(4\text{-}FC_6H_4)_3P$	$(CH_3CO)_2O$	37	4	11/11[d]	1.97	145
$(4\text{-}FC_6H_4)_3P$	$(C_3H_7CO)_2O$	100	4	28/28[d]	"	"
$(2\text{-}CH_3C_6H_4)_3P$	$(C_3H_7CO)_2O$	0	4		3.08	194

[a]Determined by GC. [b] pKa values of ligands were taken from ref. 9-10. [c]Cone angle data of ligands were taken from ref. 10-12 .[d] Variable amount of the corresponding hydroxyester and some products not yet identified were also present.

As shown in Table 1 both steric and electronic effects of the phosphines and the carboxylic anhydrides control the rate and the selectivity of the reaction to give the 1,4 or 1,2 regioisomer.

As regard to phosphines, the influence of steric effects prevails over electronic factors: with large cone angles, both the regioselectivity and the reaction rate are reduced considerably. With phosphines with the same cone angle but with a different basicity, a slight change of the of reaction trend is observed: the reaction rate increases with the electron-withdrawing ability of the ligand. This could be explained with an increase of the positive charge on π-allyl complex[10] and the consequent easier attack of the carboxylate.

From the results obtained with different carboxylic anhydrides we can notice that the regioselectivity improves with the steric hindrance of anhydride and the basicity of the corresponding carboxylate.

As shown in Table 2, also the solvent plays an important role in determining the 1,4/1,2 ratio although it is difficult to find a rationale for its influence. Even if THF is not the best solvent for the reaction regioselectivity it gives the best yield (97%). Using the other solvents the yield is lower for the presence of unidentified products.

Table 2. Solvent Effect[a]. Palladium Complexes Catalized Reaction between Butadiene Monoxide and Carboxylic Anhydrides.

Solvent	**5**/**6** (% yields)[b]
THF	73/24
AcOEt	68/20
CH_2Cl_2	63/12
DCE	64/12
CH_3CN	40/30

(a) All reactions were carried out for 4 hours at 25°C using $PhMe_2P$ as ligand and $(C_3H_7CO)_2O$ as carboxylic anhydride.(b) Determined by GC.

Using CH_2Cl_2 as solvent with Ph_2MeP and $(C_3H_7CO)_2O$ the reaction regioselectivity is the highest (**5**/**6** = 17) but the yield is not satisfactory (71 %).

It is worth noting that the ratio between the cis and trans isomers of 1,4 adduct is not constant but depends to the nature of the phosphine, as shown in Table 3.

Table 3. Ligand Effect on the Ratio trans-**5**/cis-**5** isomers[(a)]. Palladium Complexes Catalized Reaction between Butadiene Monoxide and Carboxylic Anhydrides.

Ligand	trans-**5**/cis-**5**[(b)]
Ph_2MeP	9.3
$PhMe_2P$	11.3
Ph_3P	4.1
$(4\text{-}CH_3C_6H_4)_3P$	5.6
$(4\text{-}ClC_6H_4)_3P$	5.6
$(4\text{-}FC_6H_4)_3P$	4.7

[(a)] All reactions were carried out for 4 hours, in THF at 25°C in presence of $(C_3H_7CO)_2O$ as carboxylic anhydride.[(b)] Determined by GC.

Using an epoxide/palladium ratio =1400, with pivalic anhydride and PPh_2Me, 87% of epoxide is converted after 3 days with **5**/**6** ratio = 11 and yield = 75%.

In conclusion the use of anhydrides with a suitable palladium ligand phosphine allows to obtain the diesters of 2-buten-1,4-diol with high regioselectivity and good yield.

REFERENCE:

1. Deardorff D. R.; Myles D. C.; MacFerrin K. D., *Tetrahedron Lett.* **1985**, 26, 5615-5618.
2. Trost B. M.; Angle S. R., *J. Am. Chem. Soc.* **1985**, 107, 6123-6124.
3. Echavarren A. M.; Tueting D. R.; Stille J. K., *J. Am. Chem. Soc.* **1988**, 110, 4039-4041.
4. Tsuji J.; Kataoka H.; Kobayashi Y., *Tetrahedron Lett.* **1981**, 22, 2575-2578.
5. Tsuda T.; Tokai M.; Ishida T.; Seagusa T., *J. Org. Chem.* **1986**, 51, 5216-5221.
6. Suzuki M.; Oda Y.; Noyori R., *J. Am. Chem. Soc.* **1979**, 101,1623-1625.
7. Trost B. M.; Ito T.; Greenspan P., *Tetrahedron Lett.* **1993**, 34, 1421-1424.
8. Takahashi Y.; Ito T.; Sakai S.; Ishii Y., *J. Chem. Soc. Chem.. Commun.* **1970**, 1065-1066.
9. Trogler W. C.; Marzilli L. G., *Inorg. Chem.* **1975**, 14, 2942-2948.
10. Goux C.; Massacret M.; Lhoste P.; Sinou D., *Organometallics* **1995**, 14, 4585-4593
11. Tolman C. A., *Chem.. Rev.* **1977**, 77, 331-348.
12. White D.; Coville N. J., *"Advance in Organometallic Chemistry"*, Ed. Academic Press, Inc. **1994**, 36, 95-158

(*Received in UK* 31 *January* 1997; *accepted* 21 *March* 1997)