DOI: 10.1002/ejoc.200600577

# Reactivity of 1-Phenoxy-2,7-octadiene under Metathesis Conditions

**Céline Damez,[a] Sandrine Bouquillon,[a] Françoise Hénin,[a] and Jacques Muzart*[a]**

*In memory of our friend Marcial Moreno-Mañas*

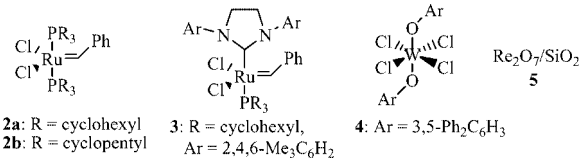
**Keywords:** Metathesis / Isomerization / Ruthenium / Rhenium / Tungsten

The metathesis of the internal double bond of 1-phenoxy-2,7-octadiene was found to be mediated by Grubbs catalysts. In the presence of rhenium or tungsten-based catalysts the reaction was found to afford *o*-substituted phenols.



## Introduction

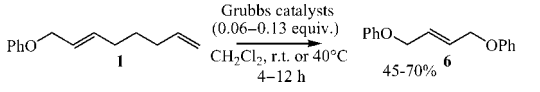
The Pd-catalyzed telomerization of butadiene with phenol affords (*E*)-1-phenoxy-2,7-octadiene (**1**),[1] and we have disclosed a recycling procedure that uses palladium supported on $KF/Al_2O_3$ as the catalyst [1 g]. Within the framework of the synthesis of bolaforms from octadienyl pentosides,[2] we examined the reactivity of **1** as a model compound in the presence of various metathesis catalysts (Scheme 1).[3] The unexpected results are reported herein.




Scheme 1.

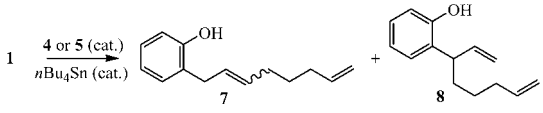
## Results

The reaction of **1** with well-known Grubbs catalysts **2a**,[4,5] **2b**[5] and **3**[6] under different experimental conditions provided products that only resulted from the metathesis of the internal double bond to afford (*E*)-1,4-diphenoxybut-2-ene (**6**) [Equation (1)]. The best result (70% yield) was obtained with 0.06 equiv. of **2a** heated at 40 °C for 4 h. We suspect that some coordination of the phenoxy moiety to the catalyst is responsible for this selectivity. Indeed, it has been reported that the course of the metathesis of olefins can be sensitive to chelation of oxygen functionalities.[3a]




(1)

These results led us to examine the use of less common catalysts **4** and **5** that, associated to $nBu_4Sn$ in some cases, have been used in metathesis reactions.[7,8] In fact, the reaction of **1**, in the presence of catalytic amounts of **4** or **5**, with or without $nBu_4Sn$, afforded a mixture of 2-(octa-2,7-dienyl)phenol (**7**) and 2-(octa-1,7-dien-3-yl)phenol (**8**) [Equation (2)]. As shown by the results collected in Table 1, the presence of $nBu_4Sn$ did not greatly modify the chemical yields, but it did have a strong influence on the **7**/**8** ratio. No reaction was observed with only $nBu_4Sn$ as the catalyst even when the reaction was heated at 85 °C. The purification of the compounds by chromatography proved to be problematic and only a mixture of (*E*)- and (*Z*)-**7** was isolated from a mixture of **7** and **8**.




(2)

2-(Octa-2,7-dienyl)phenol (**7**) and 4-(octa-2,7-dienyl)phenol have been obtained by Smutny and Chung from the Pd-catalyzed reactions of **1** with butadiene in basic media,[1c,9] and the corresponding $^1H$ NMR spectra are included in one of the reports.[1c] However, these spectra were recorded with a 60 MHz spectrometer and are of low resolution. The comparison of their spectra with our $^1H$ NMR spectroscopic data did not allow us to establish, with confidence, the *o*-substitution of the phenols obtained from **1**. Furthermore, we have not been able to reproduce Smutny's results with the use of phenol, butadiene (4 equiv.), $PdCl_2$

[a] Unité Mixte de Recherche "Réactions Sélectives et Applications", Boîte no. 44, CNRS – Université de Reims Champagne-Ardenne
B. P. 1039, 51687 Reims Cedex 2, France
E-mail: jacques.muzart@univ-reims.fr

Table 1. Reaction of **1** with Re and W catalysts.

| Catalyst | Solvent | Temp. [°C] | Time [h] | Yield of **7** + **8** [%] | Ratio of **7**/**8**[a] |
|---|---|---|---|---|---|
| **4** (0.067 equiv.) + $n$Bu$_4$Sn (0.2 equiv.) | PhCl | 85 | 48 | 77 | 3.8 |
| **4** (0.067 equiv.) | PhCl | 85 | 48 | 75 | 8.6 |
| **5** (0.017 equiv. Re) + $n$Bu$_4$Sn (0.012 equiv.) | hexane | 20 | 10 | 45 | 4.9 |
| **5** (0.02 equiv. Re) | hexane | 20 | 12 | 40 | 6.1 |

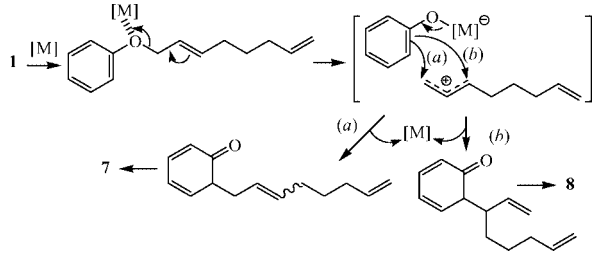
[a] Measured by $^1$H NMR spectroscopy.

(0.014 equiv.), $PPh_3$ (0.022 equiv.) and PhONa (0.041 equiv.) heated at 90 °C in THF.[9,10] Because 2D NMR experiments led to ambiguous results, we have determined the structures of **7** and **8** from comparison of their IR and $^1$H NMR spectroscopic properties with those of other compounds.

In the IR spectrum, the absorption frequency of the aromatic CH out-of-plane bending vibration is characteristic of the substitution of aryl moieties.[11] This IR band appears at 752,[12] 753, 752 and 753 cm$^{-1}$ for **7**, **8**, *o*-cresol and 2-allylphenol, respectively, whereas this absorption appears at 815 cm$^{-1}$ for *p*-cresol and 823 cm$^{-1}$ for 4-(octa-2,7-dienyl)phenol.[1c] The IR values that we obtained experimentally seem to indicate *o*-substitution of **7** and **8**. This was confirmed from the comparison of the $^1$H NMR signals of the aromatic hydrogens of *o*- and *p*-substituted phenols. *p*-Substituted phenols have a plane of symmetry and the four aromatic hydrogens gives rise to two signals as reported for *p*-cresol[13] and 4-allylphenol,[14] whereas *o*-substituted phenols produce a more complicated splitting pattern in the spectra as exemplified by *o*-cresol, 2-allylphenol, 2-(methylallyl)phenol[15] and 2-(but-3-en-2-yl)phenol.[16] Both **7** and **8** show $^1$H NMR spectroscopic data (see Experimental Section) that is in agreement with *o*-substituted phenols.

We suspected that the formation of **8** occurred by a Claisen rearrangement.[17] However, **1** was recovered almost quantitatively when heated at either 180 °C for 48 h in *N*,*N*-diethylaniline[18] or at reflux for 24 h in toluene with a Pd$^{II}$ catalyst [0.1 equiv. of $PdCl_2$ or $PdCl_2(MeCN)_2$].[19] In contrast, rapid degradation of **1** was observed with a catalytic amount of $Et_2AlCl$ (0.02 equiv.) in hexane at room temperature.[20] The use of a catalytic amount of $Pd_2dba_3$·$CHCl_3$ (0.02 equiv.) and diphenylphosphanylbutane (0.08 equiv.) in THF heated at reflux for 24 h afforded 3-phenoxy-1,7-octadiene, which results from the isomerization of $\eta^3$-allylpalladium intermediates.[21,22]

From these results, we suggest that the rearrangement of **1** is due to the Lewis acid character of the catalytic species that mediates the cleavage of the *O*-allyl bond to afford an aryloxy–metal anion and an allylic cation. Depending on the site of attack, **7** and **8** are finally afforded (Scheme 2). Strong interactions between these two ionic species could explain the selective *o*-attachment of the C8 chain whereas the selectivity of paths *a* and *b* is dependent on the nature of the catalytic system.




Scheme 2.

## Conclusions

Grubbs catalysts **1**, **2** and **3** have been shown to mediate the metathesis of the internal double bond of 1-phenoxy-2,7-octadiene to afford 1,4-diphenoxybut-2-ene. In contrast, rhenium- and tungsten-based catalysts react at the phenoxyallyl moiety to afford 2-substituted phenols.

## Experimental Section

**Ru-Catalyzed Reaction:**[5] A solution of **2a** (28.5 mg, 0.03 mmol) in $CH_2Cl_2$ (5 mL) was added to a solution of **1** (101 mg, 0.5 mmol) in $CH_2Cl_2$ (5 mL). After stirring at 40 °C for 4 h, activated charcoal was added to the mixture, stirred for 20 min and then filtered through Celite. After evaporation of the solvent under reduced pressure, flash chromatography eluted with petroleum ether/EtOAc (9:1) afforded **6** (84 mg, 70% yield) whose melting point and $^1$H NMR spectrum are in agreement with the literature data.[23]

**W-Catalyzed Reaction:**[7d] Tetra-*n*-butyltin (0.1 mL, 0.3 mmol) was added to a solution of **4** (82 mg, 0.1 mmol) in PhCl (0.5 mL). After stirring at 85 °C for 20 min, the solution was added to **1** (303 mg, 1.5 mmol) dissolved in PhCl (0.5 mL). After 48 h, the solvent was evaporated under vacuum. Diethyl ether (20 mL) was added to the residue and the mixture was washed with water and then dried with $MgSO_4$. Evaporation of the solvent followed by flash chromatography eluted with petroleum ether/EtOAc (95:5) afforded a mixture (233 mg) of **7** and **8** (**7**/**8** = 3.8 measured by $^1$H NMR spectroscopy).

**Re-Catalyzed Reaction:**[8d] $Re_2O_7/SiO_2–Al_2O_3$ (3 wt.-%) was heated at 120 °C under vacuum for 2 h to activate it before use. Tetra-*n*-butyltin (6 μL, 0.018 mmol.) was added to a suspension of $Re_2O_7/SiO_2–Al_2O_3$ (200 mg, 0.025 mmol of Re) in hexane (10 mL). The mixture was stirred for 5 min, and a solution of **1** (303 mg, 1.5 mmol) in hexane (5 mL) was added dropwise. The resulting mixture was stirred at room temperature for 10 h. After filtration through Celite and evaporation of the solvent under reduced pressure, flash chromatography eluted with petroleum ether/EtOAc

(95:5) afforded a mixture (136 mg) of **7** and **8** (**7**/**8** = 4.9 measured by $^1$H NMR spectroscopy).

**2-(Octa-2,7-dienyl)phenol (7):**[1c,9] IR (film): $\tilde{\nu}$ = 3442, 3075, 2926, 2855, 1502, 1455, 911, 752 cm$^{-1}$. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.49 (quint, $J$ = 7.5 Hz, 2 H), 1.98–2.16 (m, 4 H), 3.33–3.39 (m, 2 H), 4.93 (dd, $J$ = 0.9, 10.5 Hz, 1 H), 4.99 (dd, $J$ = 0.9, 17.1 Hz, 1 H), 5.24 (s, 1 H), 5.56–5.68 (m, 2 H), 5.79 (m, 1 H), 6.80 (m, 1 H), 6.90 (m, 1 H), 7.04–7.19 (m, 2 H) ppm. $^{13}$C NMR (62 MHz, $CDCl_3$): $\delta$ = 28.5, 31.8, 33.2, 34.3, 114.6, 115.8, 120.8, 127.8, 127.9, 129.9, 130.2, 132.8, 138.6, 154.3 ppm.

**2-(Octa-1,7-dien-3-yl)phenol (8):** IR (film): $\tilde{\nu}$ = 3386, 3075, 2926, 2855, 1708, 1513, 1455, 1241, 911, 831, 753 cm$^{-1}$. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.75 (dd, $J$ = 7.7, 8.0 Hz, 2 H), 1.94–2.12 (m, 4 H), 3.53 (m, 1 H), 4.88–5.04 (m, 2 H), 5.06–5.18 (m, 2 H), 5.24 (s, 1 H), 5.76 (m, 1 H), 5.98 (m, 1 H), 6.71 (m, 1 H), 6.86 (m, 1 H), 7.02–713 (m, 2 H) ppm. $^{13}$C NMR (62 MHz, $CDCl_3$): $\delta$ = 26.8, 29.7, 33.7, 43.5, 114.9, 115.0, 116.2, 120.9, 127.5, 128.5, 132.8, 138.7, 141.4, 153.9 ppm.

## Acknowledgments

This work was supported by the "Contrat d'Objectifs" in "Europol'Agro" framework (Glycoval program). We are grateful to the Public Authorities of Champagne-Ardenne for a fellowship to C D and material funds.

[1] a) E. J. Smutny, *J. Am. Chem. Soc.* **1967**, *89*, 6793–6794; b) S. Takahashi, T. Shibano, N. Hagihara, *Bull. Chem. Soc. Jpn.* **1968**, *41*, 454–460; c) E. J. Smutny, H. Chung, *Prepr. Pap. - Am. Chem. Soc. Div. Pet. Chem.* **1969**, *14*, B112–B122; d) K. Kaneda, H. Kurosaki, M. Terasawa, T. Imanaka, S. Teranishi, *J. Org. Chem.* **1981**, *46*, 2356–2362; e) A. Krotz, F. Vollmüller, G. Stark, M. Beller, *Chem. Commun.* **2001**, 195–196; f) B. Blanco, M. Brissart, M. Moreno-Mañas, R. Pleixats, A. Mehdi, C. Reyé, S. Bouquillon, F. Hénin, J. Muzart, *Applied Catal. A: General* **2006**, *297*, 117–124; g) B. Estrine, R. Soler, C. Damez, S. Bouquillon, F. Hénin, J. Muzart, *Green Chem.* **2003**, *5*, 686–689.

[2] C. Damez, PhD Thesis, Reims, **2006**.

[3] For reviews on metathesis, see a) S. Blechert, S. J. Connon, *Angew. Chem. Int. Ed.* **2003**, *42*, 1900–1923; b) R. R. Schrock, A. H. Hoveyda, *Angew. Chem. Int. Ed.* **2003**, *42*, 4592–4633; c) A. H. Hoveyda, D. G. Gillingham, J. J. van Veldhuizen, O. Kataoka, S. B. Garber, J. S. Kingsbury, J. P. A. Harrity, *Org. Biomol. Chem.* **2004**, *2*, 8–23; d) R. R. Schrock, *J. Mol. Catal. A* **2004**, *213*, 21–30; e) A. Deiters, S. F. Martin, *Chem. Rev.* **2004**, *104*, 2199–2238; f) R. H. Grubbs, *Tetrahedron* **2004**, *60*, 7117–7140; g) D. Astruc, *New J. Chem.* **2005**, *29*, 42–56; h) K. C. Nicolaou, P. G. Bulger, D. Sarlah, *Angew. Chem. Int. Ed.* **2005**, *44*, 4490–4527; i) C. Bruneau, P. H. Dixneuf, *Angew. Chem. Int. Ed.* **2006**, *45*, 2176–2203.

[4] P. Schwab, M. B. France, J. W. Ziller, R. H. Grubbs, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2039–2041.

[5] P. Schwab, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1996**, *118*, 100–110.

[6] S. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953–956.

[7] a) F. Quignard, M. Leconte, J. M. Basset, *J. Mol. Catal.* **1985**, *28*, 27–32; b) F. Quignard, M. Leconte, J. M. Basset, *J. Mol. Catal.* **1986**, *36*, 13–29; c) C. van Schalkwyk, H. C. M. Vosloo, J. A. K. du Plessis, *J. Mol. Catal. A* **1998**, *133*, 167–173; d) G. Descotes, J. Ramza, J. M. Basset, S. Pagano, E. Gentil, J. Banoub, *Tetrahedron* **1996**, *52*, 10903–10920; e) B. B. Marvey, J. A. K. du Plessis, H. C. M. Vosloo, *J. Mol. Catal. A* **2004**, *213*, 151–157.

[8] a) R. H. A. Bosma, G. C. N. Van Den Aardweg, J. C. Mol, *J. Organomet. Chem.* **1983**, *255*, 159–171; b) A. Ellison, A. K. Coverdale, P. F. Dearing, *Appl. Catal.* **1983**, *8*, 109–121; c) X. Xiaoding, J. C. Mol, *J. Chem. Soc., Chem. Commun.* **1985**, 631–633; d) B. B. Marvey, J. A. K. du Plessis, H. C. M. Vosloo, J. C. Mol, *J. Mol. Catal. A* **2003**, *201*, 297–308.

[9] E. J. Smutny, US Patent 3 518318 [*Chem. Abstr.* **1970**, *72*, 132047].

[10] This is in accordance with the results of Beller's team who have observed that the Pd-catalyzed telomerization of butadiene with phenol yields only the corresponding *O*-allylated ethers.[1e] In contrast, other phenols, particularly 2-naphthol, afford the *C*- and *O*-allylated compounds[1e].

[11] a) R. T. Conley, *Infrared Spectroscopy*, 2nd ed., Allyn and Bacon, Boston, **1972**, pp. 112–117; b) M. Hesse, H. Meier, B. Zeeh, *Méthodes Spectroscopiques pour la Chimie Organique*, Masson, Paris, **1997**, pp. 66–68.

[12] According to Smutny and Chung, this IR band appears at 749 cm$^{-1}$.[1c]

[13] K. Tori, Y. Yoshimura, *Tetrahedron Lett.* **1973**, *14*, 3127–3130.

[14] M. R. Agharahimi, N. A. LeBel, *J. Org. Chem.* **1995**, *60*, 1856–1863.

[15] C. D. Selassie, A. J. Shusterman, S. Kapur, R. P. Verma, L. Zhang, C. Hansch, *J. Chem. Soc., Perkin Trans. 2* **1999**, 2729–2733.

[16] R. M. Jones, R. W. Van De Water, C. C. Lindsey, C. Hoarau, T. Ung, T. R. R. Pettus, *J. Org. Chem.* **2001**, *66*, 3435–3441.

[17] For reviews, see a) M. Hiersemann, L. Abraham, *Eur. J. Org. Chem.* **2002**, *67*, 1461–1471; b) U. Nubbemeyer, *Synthesis* **2003**, 961–1008; c) A. M. M. Castro, *Chem. Rev.* **2004**, *104*, 2939–3002.

[18] J. W. Benbow, R. Katoch-Rouse, *J. Org. Chem.* **2001**, *66*, 4965–4972.

[19] a) J. L. van der Baan, F. Bickelhaupt, *Tetrahedron Lett.* **1986**, *27*, 6267–6270; b) A. S. R. Anjaneyulu, B. M. Isaa, *J. Chem. Soc., Perkin Trans. 1* **1991**, 2089–2094; c) K. Itami, D. Yamazaki, J. Yoshida, *Org. Lett.* **2003**, *5*, 2161–2164; d) C. Nevado, A. M. Echavarren, *Tetrahedron* **2004**, *60*, 9735–9744; e) S. W. Youn, J. I. Eeon, *Org. Lett.* **2005**, *7*, 3355–3358.

[20] a) F. M. Sonnenberg, *J. Org. Chem.* **1970**, *35*, 3166–3167; b) B. M. Trost, F. D. Toste, *J. Am. Chem. Soc.* **1998**, *120*, 815–816.

[21] J. Muzart, J.-P. Genêt, A. Denis, *J. Organomet. Chem.* **1987**, *326*, C23–C28.

[22] Pd$^0$-catalyzed isomerization of allyl phenyl ethers to allylphenols has been recently reported, see E. Kuntz, A. Amgoune, C. Lucas, G. Godard, *J. Mol. Catal. A: Chem.* **2006**, *244*, 124–138. The Pd$^0$-catalyzed *C*-allylation of naphthols has also been disclosed, see a) C. Goux, M. Massacret, P. Lhoste, D. Sinou, *Organometallics* **1995**, *14*, 4585–4593; b) Y. Tada, A. Satake, I. Shimizu, A. Yamamoto, *Chem. Lett.* **1996**, 1021–1022.

[23] F. Bigi, G. Casiraghi, G. Casnati, G. Sartori, *Tetrahedron* **1983**, *39*, 169–174.

Received: July 6, 2006
Published Online: August 28, 2006