Pergamon

Tetrahedron Letters 41 (2000) 8259–8262

TETRAHEDRON LETTERS

Palladium-catalyzed arylation of butadiynes

Gerald Dyker,[a,*] Stefan Borowski,[a] Gerald Henkel,[a] Andreas Kellner,[b] Ina Dix[c] and Peter G. Jones[c]

[a]*Institut für Synthesechemie, Fachbereich 6, Gerhard-Mercator-Universität Duisburg, Lotharstraße 1, D-47048 Duisburg, Germany*

[b]*Institut für Organische Chemie der Technischen Universität Braunschweig, Hagenring 30, D-38106 Braunschweig, Germany*

[c]*Institut für Anorganische Chemie und Analytische Chemie der Technischen Universität Braunschweig, Hagenring 30, D-38106 Braunschweig, Germany*

Received 23 August 2000; accepted 4 September 2000

Abstract

Diarylbutadiynes **1** undergo a palladium-catalyzed coupling reaction with aryl halides **2** to give tetraarylbutatrienes **3**, which may further react to benzofulvenes **6** depending on the reaction temperature and the type of aryl groups.

Keywords: arylation; butadiynes; butatrienes; domino processes; palladium catalysis.

The carbopalladation of disubstituted alkynes is known as the initial key step of a variety of palladium-catalyzed domino processes leading to annulated ring systems.[1] In a preceding report we presented the synthesis of 9,10-diarylphenanthrenes from diarylalkynes and iodoarenes: the stereochemical lability of intermediary vinyl palladium species was responsible for the formation of several isomeric products.[1c] We became interested in the analogous arylation of diarylbutadiynes **1**, since for this type of unsaturated substrates the regioselectivity of the carbopalladation step and the kinetic stability of the resulting vinyl palladium complexes were a priori unclear; therefore the outcome of this type of reaction was difficult to predict.

Under moderate reaction conditions (80°C, Table 1, entry 2) a 53% yield of tetraphenylbutatriene (**3a**, $A^1 = A^2 = Ph$) was obtained from diphenylbutadiyne (**1a**) and an excess of iodobenzene (**2a**). The formation of this rather surprising main product clearly indicates the regioselectivity of the first carbopalladation step and is in accord with the mechanistic pathway in Scheme 1: a vinyl palladium species **4** is formed with two geminal aryl groups. The lifetime of this species is obviously not sufficient for a cyclometallation at the neighboring aryl group, a pathway which would lead to the formation of a phenanthrene moiety.[1c] Presumably a

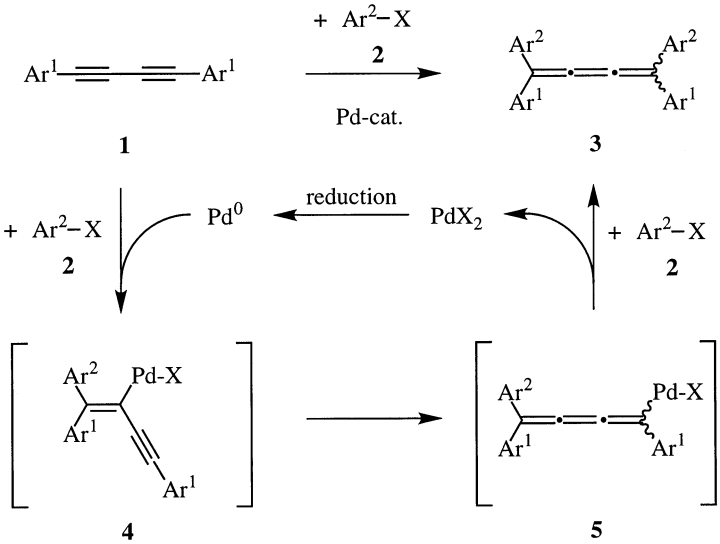
* Corresponding author. Tel: +208-379-2831; fax: +208-379-4192; e-mail: dyker@uni-duisburg.de

0040-4039/00/$ - see front matter
PII: S0040-4039(00)01474-X

Table 1
Pd-catalyzed coupling reactions of diarylbutadiynes **1** with aryl halides **2**[a]

Entry	**1**: Ar^1	**2**: Ar^2; X	Base	*T* (°C)	*t* (d)	Yield[b](%):	**3**	**6**
1	**1a**: phenyl	**2a**: phenyl; I	Et_3N	60	2.5		16	–
2	**1a**: phenyl	**2a**: phenyl; I	Et_3N	80	2.5		53	trace
3	**1a**: phenyl	**2a**: phenyl; I	NaOAc	100	2.5		37	41
4	**1a**: phenyl	**2a**: phenyl; I	NaOAc	120	2.5		–	52
5	**1b**: 1-naphthyl	**2b**: 1-naphthyl; I	Et_3N	120	2.5		64[c]	–
6	**1c**: 9-anthryl	**2c**: 9-anthryl; I	Et_3N	95	2.5		–	–
7	**1a**: phenyl	**2b**: 1-naphthyl; Br	Et_3N	80	3		15[d]	–
8	**1a**: phenyl	**2d**: mesityl[e]; Br	Et_3N	110	15		15[d]	–
9	**1a**: phenyl	**2c**: 9-anthryl; Br	Et_3N	110	14		17[d]	–

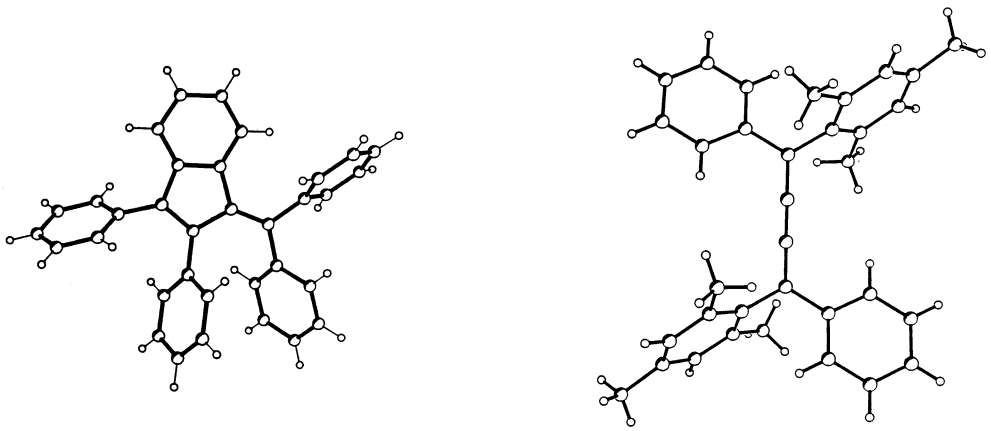
[a] Reaction conditions: 1 mmol of **1**, 5 mmol of **2**, 5 mol-% of $Pd(OAc)_2$, 10 mol-% of PPh_3, 5 mmol of NaOAc or 4 ml of Et_3N, 10 ml of dry DMF.
[b] Yields of the isolated products are given.
[c] Twice the amount of catalyst and ligand applied.
[d] Mixture of stereoisomers.
[e] 2,4,6-Trimethylphenyl.



Scheme 1. Mechanistic pathway for the formation of butatriene **3** from butadiyne

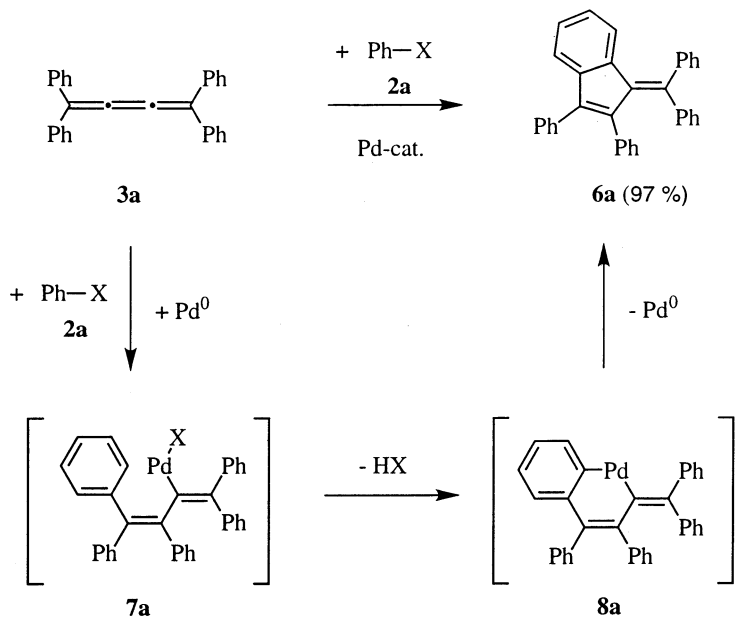
rearrangement to **5** takes place instead (such a rearrangement has some precedent in the double silylation of bis(trimethylsilyl)butadiyne to tetrakis(trimethylsilyl)butatriene).[2] The domino process is terminated by a coupling reaction of Pd-complex **5** with a second equivalent of the aryl halide **2**. Irrespective of whether the latter reaction step proceeds via a Pd^{IV}-intermediate[3] (by direct oxidative addition of **2** to the Pd^{II}-intermediate **5**) or involves a ligand exchange reaction[4] between **5** and an aryl palladium halide, the formation of PdX_2 has to be taken into account. Therefore, an 'in situ' reduction to the active Pd^0-catalyst is necessary in each catalytic circle. Also, the Pd-catalyzed Ullmann coupling reaction[5] (aryl halide is transformed to biaryl), which is observed as a competing reaction, affords such a reductive step and is known to be feasible in the presence of DMF as solvent.

At elevated temperatures (100–120°C) butatriene **3a** is replaced by the benzofulvene **6a**[6] as the final product of the domino coupling process (52% yield, entries 3 and 4 of Table 1), unambiguously identified by a X-ray structure analysis (Fig. 1).[7] With preformed **3a** as starting material the yield of **6a** increased to 97% (Scheme 2). This reaction is easily explained by a carbopalladation of the central double bond of **3a** to give intermediate **7a**, followed by cyclopalladation to **8a** and the final reductive elimination.



6a **3a/d**

Figure 1. X-ray structure analysis of selected coupling products



Scheme 2. Mechanistic pathway for the formation of benzofulvene **6a** from butatriene **3a**

In order to test scope and limitations of the domino coupling process, we varied the aryl groups of starting materials **1** and **2**. The 1-naphthyl substituted coupling components **1b** and **2b**

led to the isolation of the tetranaphthylbutatriene **3b** in acceptable yield (Table 1, entry 5). In contrast, the 9-anthryl substituted starting materials **1c** and **2c** gave no coupling products (Table 1, entry 6).

Entries 7–9 result in butatrienes **3** with mixed substituents[8] and are of importance for studying the stereoselectivity of the coupling process: according to NMR and MS data mixture of the *cis* and the *trans* isomers are obtained in all cases. Since the initial carbopalladation step should proceed in a *syn*-manner, the *cis–trans* isomerization presumably takes place at the stage of the vinyl palladium intermediates **4** and **5**; the stereochemical lability of similar palladium species has been demonstrated previously.[1c]

Details of the stereoselectivity of this process are to be investigated; however, in the case of butatriene **3a**/**d** with two mesityl substituents a fraction of a pure stereoisomer was obtained by crystallization, identified as the *trans* isomer by an X-ray structure analysis (Fig. 1).[7,9] Bond lengths of the central butatriene unit are virtually identical with those of the tetraphenyl-substituted derivative **3a**.[10,11] The two sterically demanding mesityl substituents in structure **3a**/**d** are of course more twisted with respect to the butatriene unit than the neighboring phenyl groups. For the two distinct positions in the elemental cell torsion angles of 68 and 70° are found for the mesityl groups, and 24 and 1° for the phenyl groups, respectively.

Acknowledgements

Financial support of the *Fonds der Chemischen Industrie* is gratefully acknowledged. We are indebted to Degussa AG for a generous donation of palladium acetate.

References

1. (a) Wu, G.; Rheingold, A. L.; Geib, S. J.; Heck, R. F. *Organometallics* **1987**, *6*, 1941–1946; (b) Dyker, G. *J. Org. Chem.* **1993**, *58*, 234–238; (c) Dyker, G.; Kellner, A. *Tetrahedron Lett.* **1994**, *35*, 7633–7636; (d) Larock, R. C.; Tian, Q. *J. Org. Chem.* **1998**, *63*, 2002–2009; (e) Larock, R. C. *J. Organomet. Chem.* **1999**, *576*, 111–124; (f) Dyker, G.; Siemsen, P.; Sostmann, S.; Wiegand, A.; Dix, I.; Jones, P. G. *Chem. Ber./Recueil* **1997**, *130*, 261–265.
2. Kusumoto, T.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3103–3110.
3. (a) Canty, A. J. *Platinum Met. Rev.* **1993**, *37*, 2–7; (b) Canty, A. J. *Acc. Chem. Res.* **1992**, *25*, 83–90.
4. (a) Ozawa, F.; Hidaka, T.; Yamamoto, T.; Yamamoto, A. *J. Organomet. Chem.* **1987**, *330*, 253; (b) Ozawa, F.; Fujimori, M.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1986**, *5*, 2144.
5. Dyker, G.; Kellner, A. *J. Organomet. Chem.* **1998**, *555*, 141–144.
6. Valette, P. *C.R. Acad. Sci.* **1951**, *12*, 537–567.
7. X-ray data of compounds **3a**/**d** and **6a** have been deposited at the Cambridge Crystallographic Data Centre (deposition numbers CCDC-148192 and CCDC-148624, respectively). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ [Fax. (internat.) +44-1223/336033; e-mail: deposit@ccdc.cam.ac.uk].
8. (a) Kuhn, R.; Jahn, J. *Chem. Ber.* **1953**, *86*, 759-763; (b) Edinger, J. M.; Sisenwine, S. F.; Day, A. R. *J. Org. Chem.* **1971**, *36*, 3614–3619.
9. For X-ray structure analyses of other tetraarylbutatrienes, see: Weber, E.; Seichter, W.; Wang, R.-J.; Mak, T. C. W. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 659–667.
10. Berkovitch-Yellin, Z.; Leiserowitz, L. *Acta Crystallogr., Sect. B* **1977**, *33*, 3657.
11. For an early synthesis of **3a**, see: Kuhn, R.; Wallenfels, K. *Ber. Dtsch. Chem. Ges.* **1938**, *71*, 783–790.

.