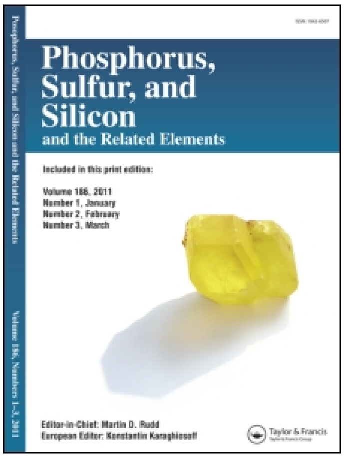


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

RAPID AND EFFICIENT PHOSPHONATION OF ARYL HALIDES CATALYSED BY PALLADIUM UNDER MICROWAVES IRRADIATION

Didier Villemin[a]; Paul-Alain Jaffrès[a]; Fabrice Siméon[a]
[a] Ecole Nationale Supérieure d'Ingenieurs de Caen (ISMRA), Université de Caen, Caen cedex, France

To cite this Article Villemin, Didier , Jaffrès, Paul-Alain and Siméon, Fabrice(1997) 'RAPID AND EFFICIENT PHOSPHONATION OF ARYL HALIDES CATALYSED BY PALLADIUM UNDER MICROWAVES IRRADIATION', Phosphorus, Sulfur, and Silicon and the Related Elements, 130: 1, 59 — 63

To link to this Article: DOI: 10.1080/10426509708033697

URL: http://dx.doi.org/10.1080/10426509708033697

Phosphorus, Sulphur, and Silicon, 1997, Vol. 130, pp. 59–63
Reprints available directly from the publisher
Photocopying permitted by license only

RAPID AND EFFICIENT PHOSPHONATION OF ARYL HALIDES CATALYSED BY PALLADIUM UNDER MICROWAVES IRRADIATION

DIDIER VILLEMIN*, PAUL-ALAIN JAFFRÈS and FABRICE SIMÉON

Ecole Nationale Supérieure d'Ingenieurs de Caen (ISMRA), Université de Caen, UMR CNRS 6507, 6 Boulevard du Maréchal Juin, F-14050 Caen cedex, France

(Received 14 May 1997)

Diethyl arylphosphonates are efficiently and rapidly prepared from aryl halides, by a palladium catalysis, performed in a Teflon autoclave under microwave radiation generated by a commercial microwave oven.

Keywords: microwaves irradiation; arylphosphonates; palladium catalysis

INTRODUCTION

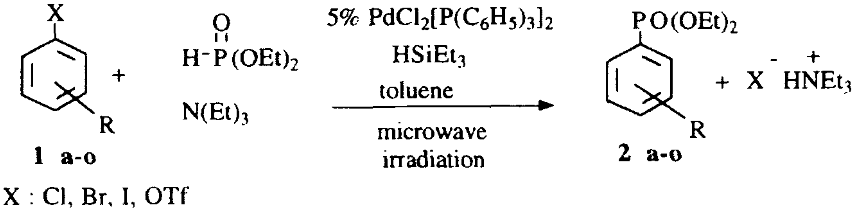
Although many organometallic complexes were efficiently obtained under microwave radiation,[1] homogeneous catalysed reactions by organometallic complexes were up to now, seldomly used.[2] The air sensitive complexes, prepared by Mingos, have been synthesized in a commercially available Teflon-autoclaves (design for mineralisation) under microwave in a focused microwave cavity. This technical needs expansive microwave generator. We report herein a rapid synthesis of diethyl aryl phosphonates, catalysed by palladium in a Teflon autoclave under microwave irradiation generated by a commercial microwave oven.[3]

RESULTS AND DICUSSION

The synthesis of arylphosphonates is of considerable current interest in that these are phosphonic acids precursors, which can be used for their water-soluble properties[4] and for the synthesis of mixed organic-inorganic materials.[5] Arylphos-

---

*Corresponding author.



SCHEME 1

phonates are commonly prepared by three methods: (a) Photoinitiated reaction of aryl halide with phosphites salts.[6] The main disadvantages of this method is the necessity of using a large excess of phosphite. (b) Reaction of aryl halide with trialkylphosphite catalysed by nickel (II), takes place under drastic conditions.[7] (c) Reaction between aryl halide and dialkylphosphite,[8] catalysed by palladium (0) complexes is efficient but the time required is long (on avarage 10 hours).

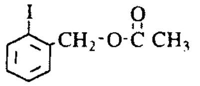
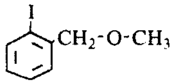
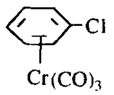
We reported that the rate of this last reaction can be dramatically enhanced if the reaction takes place in a Teflon autoclave[3] under microwave irradiation. We use the air stable[9] dichlorobis(triphenylphosphine)palladium (II) as a precursor of the palladium catalyst. The air sensitive catalyst was obtained *in situ* in the autoclave by the reduction of the precursor by triethylsilane. The reduction begins with irradiation in the Teflon autoclave and the colour of the solution, in the Teflon autoclave, turns to black (scheme 1).

The reaction conditions and yields of the various products obtained are reported in Table I. The reactions with aryl iodides gave generally good yields except for the hindered *ortho* substituted aryl iodide (**1j**, **1k**, and **1l**). We want to stress that this method has a simple workup procedure and the reaction times are very short.

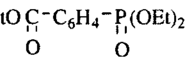
We used also other halides as leaving group such as bromide and chloride. In agreement with classical conditions, the reaction is slower with bromide than with iodide (**1b** and **1n**). With chlorobenzene no reaction was observed. We have already described the possibility to activate C-Cl bonds in a palladium catalysis process by coordination of a tricarbonylchromium moiety on chlorobenzene.[10] This process is nowadays well used in synthesis.[11] We observed the easy phosphonation (**1o**) of chlorobenzenetricarbonylchromium under microwave irradiation without decomposition of the complex.[12–13] This reaction occurred also under classical heating according to an Arbusov type reaction with the same yield (81 %) but after 7 hours at reflux.[14] Recently compound (**2o**) was synthesised by the reaction of chromium hexacarbonyl with diethylbenzenephosphonate (34 % yield; 48 h at reflux).[15]

TABLE I

Phosphonation of Ar-X (X = I, Br, Cl, OSO_2CF_3) under microwave irradiation.

	Ar 1	X	Time min. (power W)	Yield % (1) 2	^{31}P NMR
a	C_6H_5-	I	9(490)	87	18.7
		Cl	15(490)	0	
b	4-CH_3-C_6H_4-	I	11(490)	91	19.4
		Br	11(490)	53	
		Br	22(455)	65	
		O-SO_2-CF_3	10(350)	31	
c	4-CH_3O-C_6H_4-	I	9(490)	96	17.5
e	4-Br-C_6H_4-	I	12(490)	60	17.6
f	4-Cl-C_6H_4-	I	13(490)	97	17.4
g	4-H_2OC-C_6H_4-	I	4((100)	13(2)	17.2
h	4-CH_3-O-CO-C_6H_4-	I	11(490)	78	16.9
i	3-CH_3-O-CO-C_6H_4-	I	9(490)	80	17.0
j	2-CH_3-O-CO-C_6H_4-	I	15(490)	trace	15.9
k		I	9(520)	31	17.8(4)
l		I	13(490)	48	18.4(4)
m	4-CH_3-CO-NH-C_6H_4-	I	3(350)	46(3)	18.7
n	4-CH_3SO_2-O-C_6H_4-	Br	19(390)	62	16.8(4)
o		Cl	8(490)	80	16.1(4)

(1) After purification

(2) Solvent DMF and final product is :4-EtO  $\underset{O}{\overset{\|}{C}}-C_6H_4-\underset{O}{\overset{\|}{P}}(OEt)_2$

(3) Solvent: acetonitrile

(4) ^1H and ^{13}C NMR spectra see notes. [12] and [13].

Triflate was used previously as a leaving group for the synthesis of arylphosphonates.[16] Under microwave irradiation, the reaction occurred (**1b**) but the kinetics seems to be slow and so only a poor yield is obtained.

In conclusion, although the yields under classical conditions and under microwave irradiation were often comparable, the reaction rate were generally dramatically increased and the workup was very simple. The method makes use of commercially available apparatus design for mineralisation and does not need expensive focused microwave cavity.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded on a BRUKER AC 250 spectrometer in $CDCl_3$ as solvent. The spectra were measured with $SiMe_4$ as inernal standard. ^{31}P NMR was recorded on a BRUKER WP 80 SY with H_3PO_4 as external standard.

General Procedure

To bis(triphenylphosphine)palladium dichloride (64 mg; $9.2.10^{-2}$ mmol) placed in a 50 ml Savilex Teflon autoclave under argon atmosphere triethylsilane (0.01 ml; $9.2.10^{-2}$ mmol), aryl halide (1.83 mmol), diethylphosphite (0.28 g; 2.02 mmol) and triethylamine (0.22 g; 2.2 mmol) in toluene (2 ml) were added into the autoclave under an argon flow. The autoclave was closed and irradiated in a commercial microwave cavity[3] with sequence of 1 min each time until the time indicated in the Table I was reached. After cooling to room temperature, 20 ml of diethylether were added and the ammonium salt was removed by filtration. The solvent was removed and the residue was purified by Kugelrohr distillation or by column chromatography on silica gel (dichloromethane/ethanol: 98/2).

References

[1] D. M. P. Mingos and D. R. Baghurst, *Chem. Soc. Rev.*, **20**, 1 (1991); A. G. Whittaker and D. M. P. Mingos, *J. Microw. Pow. Electr. Energ.*, **30**, 27 (1995); S. Caddick, *Tetrahedron*, **51**, 10403 (1995).

[2] F. Adamek and M. Hajek, *Tetrahedron Lett.*, **33**, 2039 (1992); E. M. Gordon, D. C. Gaba, K. A. Jebber and D. M. Zacharias, *Organometallics*, **12**, 5020 (1993); M. Larhed and A. Hallberg, *J. Org. Chem.*, **61**, 9582 (1996).

[3] We used a Savilex autoclave and a commercial microwave oven Toshiba ER 8930.

[4] T. L. Schull, J. C. Fettinger and D. A. Knight, *J. Chem. Soc. Chem. Commun.*, 1487 (1995); S. Lelièvre, F. Mercier and F. Mathey, *J. Org. Chem.*, **61**, 3531 (1996).

[5] P. A. Jaffrès, Thèse de Doctorat de Chimie, Université de Caen, France (1996).

[6] J. F. Bunnett and R. H. Weisis, *Org. Synth.*, **58**, 134 (1978); J. J. Bulot, E. E. Aboujaoude, N. Collignon and P. Savignac, *Phosphorus and Sulfur*, **21**, 197 (1984).

[7] P. Tavs, *Chem. Ber.*, **103**, 2428 (1970).

[8] T. Hirao, T. Masunaga, N. Yamada, Y. Ohshiki and T. Agawa, *Bull. Chem. Soc. Jpn.*, **55**, 909 (1982).

[9] P. Roffia, F. Conti and G. Gregori, *Chem. Ind. (Milan)*, **53**, 361 (1971).

[10] D. Villemin and S. Endo, *J. Organometal. Chem.*, **283**, C10 (1985).

[11] J. F. Carpentier, L. Pamart, L. Maciewjski, Y. Casttanet, J. Brocard and A. Mortreux, *Tetrahedron Lett.*, **37**, 167 (1996). J. F. Carpentier, F. Pettit, A. Mortreux, V. Dufaud, J. M. Basset and J. Thivolle-Cazat, *J. Mol. Cat.*, **81**, 1 (1993).

[12] ^{1}H NMR spectra of new products. **2k**: 1,33 (d; $^{3}J_{HH}$ = 7.1 Hz; $C\mathbf{H}_3CH_2O$; 6H); 2.15 (s; CO-C**H**$_3$; 3H); 4.10 (m; $CH_3C\mathbf{H}_2O$; 4H); 5.44 (s; -C**H**$_2$-O-; 2H); 7.4–7.7 (m; 3H); 7.9 (dd; $^{3}J_{HH}$ = 7.6 Hz; $^{3}J_{HP}$ = 14.3 Hz; **H**$_6$; 1H); **2l**: 1.33 (d; $^{3}J_{HH}$ = 7.1 Hz; $C\mathbf{H}_3CH_2O$; 6H); 3.46 (s; O-C**H**$_3$; 3H); 4.10 (m; $CH_3C\mathbf{H}_2O$; 4H); 4.78 (s; -C**H**$_2$-O-; 2H); 7.36 (dt; $^{3}J_{HH}$ = $^{3}J_{HH}$ = 7.0 Hz; $^{4}J_{HP}$ = 2.2 Hz; **H**$_4$; 1H); 7.5–7.7 (m; **H**$_3$ et **H**$_5$; 2H); 7.92 (ddd; $^{3}J_{HH}$ = 7.6 Hz; $^{3}J_{HP}$ = 14.3 Hz; $^{4}J_{HH}$ = 2.2 Hz; **H**$_6$; 1H); **2n**: 1.34 (d; $^{3}J_{HH}$ = 7.1 Hz; $C\mathbf{H}_3CH_2O$; 6H); 3.20 (s; $C\mathbf{H}_3SO_2$; 3H); 4.13 (m; $CH_3C\mathbf{H}_2O$; 4H); 7.40 (dd; $^{3}J_{HH}$ = 8.5 Hz; $^{4}J_{HP}$ = 3.4 Hz; **H**$_2$ et **H**$_6$); 7.90 (dd; $^{3}J_{HH}$ = 8.5 Hz; $^{3}J_{HP}$ = 12.8 Hz; **H**$_3$ et **H**$_5$); **2o**: 1.38 (t; $^{3}J_{HH}$ = 7.0 Hz; $(O\text{-}CH_2\text{-}C\mathbf{H}_3)_2$; 6H); 4.2 (m; $(O\text{-}C\mathbf{H}_2\text{-}CH_3)_2$; 4H); 5.14 (ddd; $^{3}J_{HH}$ = $^{3}J_{HH}$ = 6.2 Hz; $^{4}J_{HP}$ = 2.7 Hz; 2H; **H**$_3$); 5.58 (t; $^{3}J_{HH}$ = 6.2 Hz; 1H; **H**$_4$); 5.79 (dd; $^{3}J_{HH}$ = 6.2 Hz; $^{3}J_{HP}$ = 9.1 Hz; 2H; **H**$_2$)

[13] ^{13}C NMR spectra of new products. **2k**: 16.36 (d; $^{3}J_{CP}$ = 6.3 Hz; $(O\text{-}CH_2\text{-}\mathbf{C}H_3)_2$); 62.31 (d; $^{2}J_{CP}$ = 5.4 Hz; $(O\text{-}\mathbf{C}H_2\text{-}CH_3)_2$); 64.12 (d; $^{3}J_{CP}$ = 3.6 Hz; -**C**H$_2$-O-CO); 126.56 (d; $^{1}J_{CP}$ = 183.1 Hz; **C**$_1$); 127.70 and 128.83 (2d; $^{3}J_{CP}$ = 14.4 Hz; **C**$_3$ and **C**$_5$); 132.78 (d; $^{4}J_{CP}$ = 2.7 Hz; **C**$_4$); 134.19 (d; $^{2}J_{CP}$ = 9.9 Hz; **C**$_6$); 139.43 (d; $^{2}J_{CP}$ = 9.9 Hz; **C**$_2$); 170.62 (s; **C**(O)); **2l**: 16.39 (d; $^{3}J_{CP}$ = 6.3 Hz; $(O\text{-}CH_2\text{-}\mathbf{C}H_3)_2$); 58.68 (s; O-**C**H$_3$); 62.19 (d; $^{2}J_{CP}$ = 5.4 Hz; $(O\text{-}\mathbf{C}H_2\text{-}CH_3)_2$); 72.09 (d; $^{3}J_{CP}$ = 2.7 Hz; -**C**H$_2$-O); 125.50 (d; $^{1}J_{CP}$ = 183.5 Hz; **C**$_1$); 127.02 and 128.10 (2d; $^{3}J_{CP}$ = 14.4 and 13.5 Hz; **C**$_3$ and **C**$_5$); 128.59 (d; $^{2}J_{CP}$ = 12.6 Hz; **C**$_2$); 133.73 (d; $^{2}J_{CP}$ = 9.9 Hz; **C**$_6$); 132.74 (d; $^{4}J_{CP}$ = 2.7 Hz; **C**$_4$); **2n**: 16.31 (d; $^{3}J_{CP}$ = 6.3 Hz; $(O\text{-}CH_2\text{-}\mathbf{C}H_3)_2$); 62.53 (d; $^{2}J_{CP}$ = 6.3 Hz; $(O\text{-}\mathbf{C}H_2\text{-}CH_3)_2$); 129.35 (d; $^{3}J_{CP}$ = 15.2 Hz; **C**$_3$); 132.39 (d; $^{2}J_{CP}$ = 9.87 Hz; **C**$_2$); 134.79 (d; $^{1}J_{CP}$ = 185.8 Hz; **C**$_1$); 138.75 (d; $^{4}J_{CP}$ = 3.6 Hz; **C**$_4$); 191.68 (s; **C**(O)H); **2o**: 16.40 (d; $^{3}J_{CP}$ = 6.3 Hz; $\mathbf{C}H_3\text{-}CH_2\text{-}O$); 37.92 (s; $\mathbf{C}H_3SO_2$); 62.50 (d; $^{2}J_{CP}$ = 5.5 Hz; $CH_3\text{-}\mathbf{C}H_2\text{-}O$); 122.21 (d; $^{3}J_{CP}$ = 16.2 Hz; **C**$_2$ et **C**$_6$); 128.00 (d; $^{1}J_{CP}$ = 190.2 Hz; **C**$_4$); 134.00 (d; $^{2}J_{CP}$ = 10.8 Hz; **C**$_3$ et **C**$_5$); 152.11 (d. $^{4}J_{CP}$ = 3.6 Hz; **C**$_1$)

[14] R. Chauvin, *J. Organometal. Chem.*, **387**, C1 (1990).

[15] R. W. Deemie and D. A. Knight, *Inorg. Chim. Acta*, **254**, 163 (1997).

[16] X. Lu and J. Zhu, *Synthesis*, 726 (1987).