Ruthenium- and palladium-catalyzed synthesis of polyfunctional 1,3-dienes

B. Seiller-Delevoye, C. Bruneau, and P. H. Dixneuf**

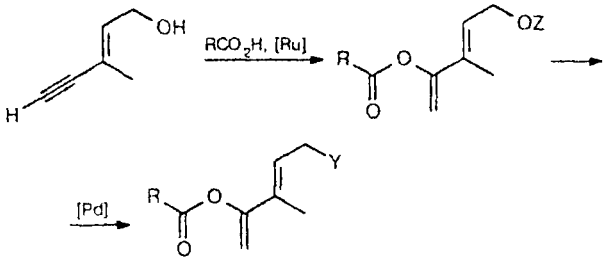
*Laboratory of Coordination Chemistry and Catalysis, National Center of Scientific Research — University of Rennes, Campus de Beaulieu, 35042 Rennes, France**

The ruthenium-catalyzed Markovnikov addition of acetic or benzoic acid to the triple bond of (*E*)-3-methylpent-2-en-4-yn-1-ol followed by acylation of the alcohol group in the diene formed under the action of low-toxic derivatives of carbonic and formic acids opens up a simple route to dienylic carbonates and formates. Activation of these esters by catalytic amounts of palladium(0) complexes under conditions of nucleophilic allylic substitution or decarboxylation affords functional dienes.

Key words: (*E*)-3-methylpent-2-en-4-yn-1-ol; carboxylic acids, addition; ruthenium(II) complexes; (*E*)-4-acetoxy(or benzyloxy)-3-methylpenta-2,4-dienyl-(2-methyl-3-oxobut-2-yl) carbonate, reaction with C- and O-nucleophiles; (*E*)-3-methyl-5-formoxypenta-1,3-dien-2-yl benzoate, decarboxylation; tetrakis(triphenylphosphine)palladium.

Conjugated dienes constitute an important class of useful building blocks for organic synthesis *via* Diels—Alder or electrophilic addition reactions.[1] They are also key substrates in reactions of C—O or C—C bond formation catalyzed by transition metal complexes especially as precursors of π-allyl metal intermediates.[2,3] However, their use in synthesis is limited by the lack of straightforward routes to polyfunctional dienes. We now report a convenient route to a variety of difunctional 1,3-dienes directly from (*E*)-3-methylpent-2-en-4-yn-1-ol based on two catalytic reactions: the ruthenium-catalyzed addition of carboxylic acid to the C≡C bond and the palladium activation of the allyl group (Scheme 1).

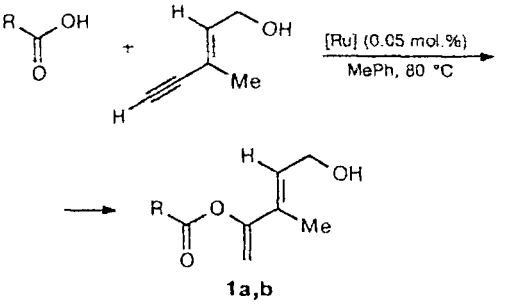
Scheme 1



Preparation of functional allylic carbonates and formates

The activation of triple bonds by ruthenium(II) complexes provides a simple and straightforward route to functional alkenes.[4,5] The Markovnikov addition of carboxylic acids to terminal alkynes is catalyzed by ruthenium(II) and gives alk-1-en-2-yl esters.[5,6] We have previously shown that the addition of carboxylic acids to conjugated enynes leads to dienyl esters.[7] The activation of (*E*)-3-methylpent-2-en-4-yn-1-ol in the presence of $[Ru(O_2CH)(CO)_2(PPh_3)]_2$ as the catalyst[4] and carboxylic acid at 80 °C made possible the preparation of acetate **1a** or benzoate **1b** in very good (>90%) yields (Scheme 2).

Scheme 2



1a,b

R = Me (**a**), Ph (**b**)
[Ru] = $[Ru(O_2CH)(CO)_2(PPh_3)]_2$

These dienyl esters have the advantage of containing a hydroxy group in the allylic position which can easily be transformed into an allylic leaving group either *via* carboxylation or acylation to give new substrates for palladium-catalyzed allylic activation.

The introduction of a carbonate or an ester functionality without using harmful derivatives such as chloroformate or acyl chloride, but with nontoxic re-

* Laboratoire de Chimie de Coordination et Catalyse, UMR 6509: CNRS — Université de Rennes, Campus de Beaulieu, 35042 Rennes, France.

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References

1. D. L. Lichtenberger, A. Rai-Chaudhuri, and R. H. Hogan, in *Inorganometallic Chemistry*, Ed. T. P. Fehlner, Plenum Press, New York—London, 1992, Ch. 5, 223.
2. (a) W. Kitching and C. W. Fong, *Organomet. Chem. Rev., A*, 1970, **5**, 281; (b) A. Wojcicki, *Acc. Chem. Res.*, 1971, **4**, 344; (c) A. Wojcicki, *Adv. Organomet. Chem.*, 1974, **12**, 31.
3. T. H. Coffield, J. Kozikowski, and R. D. Closson, *J. Org. Chem.*, 1957, **22**, 598.
4. W. R. Roper and L. J. Wright, *J. Organomet. Chem.*, 1977, 142, C1.
5. F. A. Hartmann and A. Wojcicki, *J. Am. Chem. Soc.*, 1966, **88**, 846.
6. M. Herberhold and A. F. Hill, *J. Organomet. Chem.*, 1988, 353, 243.
7. (a) R. F. Heck, *Palladium Reagents in Organic Synthesis*, Academic Press, London, 1985; (b) H. M. Colquhoun, D. J. Thompson, and M. V. Twigg, *Carbonylation*, Plenum Press, New York—London, 1991; (c) M. Beller, B. Cornils, C. D. Frohning, and C. W. Kohlpainter, *J. Mol. Catal.*, 1995, **104A**, 17.
8. (a) H. S. Klein, *J. Chem. Soc., Chem. Commun.*, 1968, 377; (b) US Pat. 3,399,146, 1968; *Chem. Abstrs.*, 1968, **69**, 86367.
9. US Pat. 4,808,697, 1989; *Chem. Abstrs.*, 1989, **111**, 134938.
10. E. Drent, J. A. M. van Broekhoven, and M. J. Doyle, *J. Organomet. Chem.*, 1991, **417**, 235.
11. (a) U. M. Dzhemilev, R. V. Kunakova, and Yu. T. Struchkov, *Dokl. Akad. Nauk SSSR*, 1980, **260**, 105 [*Dokl. Chem.*, 1980 (Engl. Transl.)]; (b) U. M. Dzhemilev and R. V. Kunakova, *J. Organomet. Chem.*, 1993, **455**, 1.
12. (a) J. Herwig, Ph.D. Thesis, RWTH, Aachen, 1994; (b) W. Keim and J. Herwig, *J. Chem. Soc., Chem. Commun.*, 1993, 1592; (c) J. Herwig and W. Keim, *Inorg. Chim. Acta*, 1994, **222**, 381; (d) J. Herwig and W. Keim, DE 4 329 932 A 1, 1995; (e) G. Pelzer, Diploma Thesis, RWTH, Aachen, 1995.
13. W. Keim, J. Herwig, and G. Pelzer, *J. Org. Chem.*, 1997, **62**, 422.
14. (a) US Pat. 5,463,145; *Chem. Abstrs.*, 1996, **124**, 88123; (b) US Pat. 5,463,144; *Chem. Abstrs.*, 1996, **124**, 88122; (c) US Pat. 5,463,146; *Chem. Abstrs.*, 1996, **124**, 569940; (d) B. Cornils, *Hydroformylation, Oxo Synthesis, Roelen Reaction*, in *New Syntheses with Carbon Monoxide*, **11**, Ed. J. Falbe, Springer, Berlin—Heidelberg—New York, 1980.
15. J. Blum and G. Scharf, *J. Org. Chem.*, 1970, **35**, 1895.
16. G. Vitzthum and E. Lindner, *Angew. Chem.*, 1971, **83**, 315.
17. W. A. Herrmann, C. Brossmer, T. Priermeier, and K. Öfele, *J. Organomet. Chem.*, 1994, **481**, 97.
18. A. Yamamoto, *J. Organomet. Chem.*, 1995, **500**, 337.
19. G. Pelzer and W. Keim, *J. Org. Chem.*, 1997, in press.
20. K. Kikukawa, T. Totoki, F. Wada, and T. Matsuda, *J. Organomet. Chem.*, 1984, **270**, 283.
21. M. Beller and K. Kühlein, *Synlett*, 1995, 441.
22. F. H. Allen and O. Kennard, *Chem. Des. Autom. News*, 1993, **8**, 31.
23. E. Lindner, J. Dettinger, H. A. Mayer, H. Kühbauch, R. Fawzi, and M. Steimann, *Chem. Ber.*, 1993, **126**, 1317.
24. G. M. Sheldrick, *Acta Crystallogr.*, 1990, **46A**, 467.
25. G. M. Sheldrick, *SHELXL-97: Program for the Refinement of Crystal Structures*, University of Cambridge, Camridge (England), 1997.

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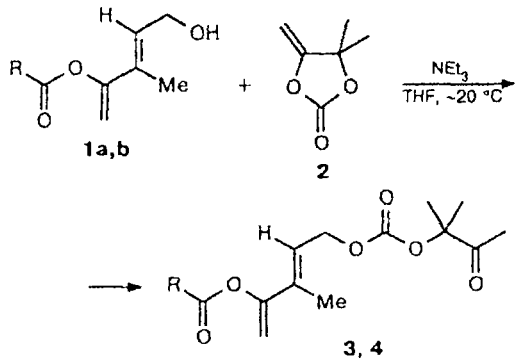
agents, presents some advantages over the classical methods based on halogenated and phosgene derivatives. The carboxylation of compounds **1a** or **1b** was carried out with cyclic carbonate **2** obtained in one step directly from CO_2.[8] Thus, the reaction of acetate **1a** or benzoate **1b** with equimolar amounts of carbonate **2** and triethylamine in THF at ~20 °C gave allylic carbonates **3** and **4** in 82 and 77% yields, respectively (Scheme 3).

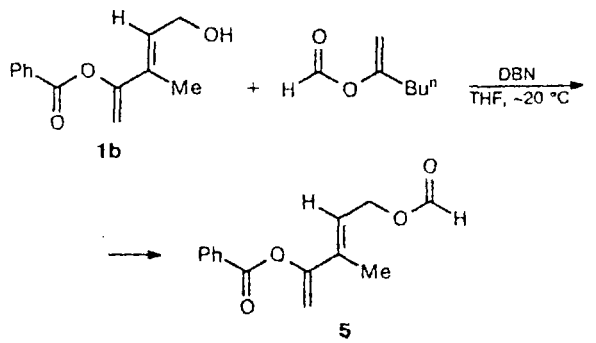
Scheme 3



R = Me (**3**), Ph (**4**)

The enol formate, but-1-en-2-yl formate, has previously been shown to be an excellent acylating reagent under neutral conditions.[9] The formylation of the benzoate **1b** was performed under mild conditions with hex-1-en-2-yl formate for 2 h at room temperature in the presence of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) (15 mol.%) resulting in mixed diester **5** in 89% yield (Scheme 4).

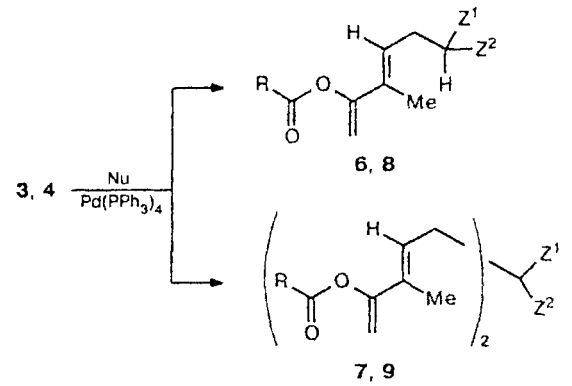
Scheme 4



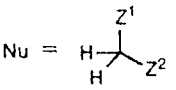
Palladium-catalyzed allylic substitution

It was expected that under very mild conditions, the activation of carbonates **3** and **4** by Pd^0 complexes could liberate CO_2, an allyl palladium species, and a α-ketoalkoxide. The latter has the potential to deprotonate carbopronucleophiles such as malonates. In fact, when carbonate **3** reacted with an equimolar amount of diethylmalonate in THF at ~20 °C for 16 h in the presence of $Pd(PPh_3)_4$ (2 mol.%), monoallylated malonate **6** was isolated in 60% yield (Scheme 5). On the other hand, when a β-diketone such as penta-2,4-dione was used as CH-acid, the reaction led only to diallylated compound **7** in 62% yield (see Scheme 5). When ketoester methyl acetoacetate was used as the pronucleophile, a mixture of compounds resulting from monoallylation (**8**, yield 61%) and diallylation (**9**, yield 31%) was obtained (see Scheme 5).

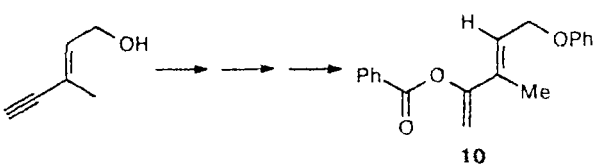
Scheme 5



6: R = Me, $Z^1 = Z^2 = CO_2Et$
7: R = Me, $Z^1 = Z^2$ = COMe
8: R = Ph, Z^1 = COMe, $Z^2 = CO_2Me$
9: R = Ph, Z^1 = COMe, $Z^2 = CO_2Me$

Nu = 

The preferred formation of compound **7** from β-diketone is explained by the faster reaction of the monoalkylated intermediate compound (analogous to **6** but with $Z^1 = Z^2$ = COMe) with the allyl palladium intermediate due to the higher concentration of the deprotonated species. Other examples of such palladium-catalyzed dialkylation of carbopronucleophiles by simple allylic derivatives have already been reported.[10,11] This reaction can be extended to other pronucleophiles rather than to compounds containing an active methylene group. 2,4-Dienyl phenyl ether **10** was obtained under similar conditions without an added base in 64% yield in the presence of $Pd(PPh_3)_4$ (2 mol.%) by the reaction of **4** with phenol.[12]

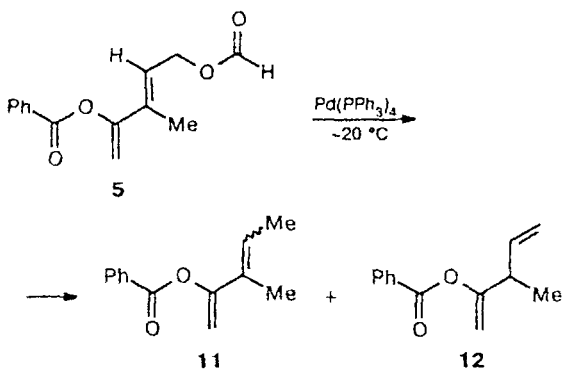


It is noteworthy that with these soft nucleophiles, the reactions *are regio- and stereoselective* as the nucleophile always adds to the *less substituted end* of the allyl species and only the *(E)-isomers* of compounds **6**—**10** are formed.

The hydrogenolysis of allylic derivatives by ammonium formate catalyzed by palladium complexes is known to afford olefins,[13] and the direct palladium activation of allylic formates[14] leads to the same type of alkenes.

Thus, with the objective of obtaining dienyl esters, we treated mixed benzoate-formate **5** (4 mmol) with $Pd(PPh_3)_4$ (2 mol.%) in THF at ~20 °C for 15 h. Indeed, a mixture of two unsaturated benzoates **11** (42%) and **12** (18%) was isolated in 60% overall yield, and their respective proportions were determined by ^1H NMR spectroscopy (Scheme 6). Compound **11**, which arises from the formation of the internal double bond, is formed as the major dienyl benzoate, which contrasts with the usual preparation of the terminal olefin as the main product upon hydrogenolysis of formates or with ammonium formate.[13,14] The formation of the conjugated diene might account for this nontypical behavior.

Scheme 6



(*E*)-4-Methylpent-2-en-4-yn-1-ol appears to be an excellent and inexpensive precursor for access to new functional 1,3-dienes *via* two catalyzed mild reactions: the regioselective Markovnikov addition of carboxylic acids followed by the regio- and stereoselective palladium-catalyzed allylation of nucleophiles. These compounds show potential for further synthetic applications as they can be involved in Diels—Alder reactions and easily converted into conjugated enones by hydrolysis of their enol ester functionality.

Experimental

^1H NMR spectra were recorded at 300 MHz on a Bruker AC 300 WPB spectrometer in $CDCl_3$, and IR spectra were recorded on a Nicolet 205 FTIR spectrometer. Mass spectra were performed on a Varian Mat 311 instrument at the CRMPO (Rennes, France), and elemental analyses were carried out by the CNRS (Vernaison, France).

Hydroxy esters **1a** and **1b** were prepared respectively from acetic or benzoic acid and commercially available (*E*)-3-methylpent-2-en-4-yn-1-ol according to Ref. 4. Carbonate **2** was prepared from carbon dioxide and 2-methylbut-3-yn-2-ol according to Ref. 8a. Hex-1-en-2-yl formate was prepared from hex-1-yne and formic acid according to Ref. 9.

Synthesis of carbonates 3 and 4. Cyclic carbonate **2** (10 mmol), hydroxy ester **1a** or **1b** (10 mmol), and triethylamine (10 mmol) were stirred in THF (5 mL) under nitrogen at ~20 °C for 20 h. Acyclic carbonates **3** and **4** were isolated by silica gel chromatography eluting with Et_2O.

(*E*)-4-Acetoxy-3-methylpenta-2,4-dien-1-yl 2-methyl-3-oxobut-2-yl carbonate (3). Yellow oil (82%). IR, ν/cm^{-1}: 1765, 1745, and 1725 (C=O); 1620 (C=C). ^1H NMR, δ: 1.48 (s, 6 H, Me_2C); 1.85 (s, 3 H, CH_3C=); 2.13 and 2.18 (2 s, 6 H, 2 CH_3CO); 4.73 (d, 2 H, OCH_2, ^3J = 6.7 Hz); 4.89 (d, 1 H, =CHH, ^2J = 2.1 Hz); 5.15 (d, 1 H, =CHH, ^2J = 2.1 Hz); 5.75 (t, 1 H, =C<u>H</u>CH_2, ^3J = 6.7 Hz).

(*E*)-Benzoyloxy-3-methylpenta-2,4-dien-1-yl 2-methyl-3-oxobut-2-yl carbonate (4). Yellow oil (77%). IR, ν/cm^{-1}: 1745 and 1725 (C=O); 1625 and 1600 (C=C). ^1H NMR, δ: 1.44 (s, 6 H, Me_2C); 1.93 (s, 3 H, CH_3C=); 2.07 (s, 3 H, CH_3CO); 4.74 (d, 2 H, OCH_2, ^3J = 7 Hz); 5.02 (d, 1 H, =CHH, ^2J = 2.2 Hz); 5.27 (d, 1 H, =CHH, ^2J = 2.2 Hz); 5.83 (t, 1 H, =C<u>H</u>CH_2, ^3J = 7 Hz); 7.44—7.60 (m, 3 H, Ph); 8.08—8.12 (m, 2 H, Ph).

(*E*)-5-Formyloxy-3-methylpenta-1,3-dien-2-yl benzoate (5). Hydroxy ester **1b** (1.09 g, 5 mmol), hex-1-en-2-yl formate (0.7 g, 5.5 mmol), and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) (0.1 mL, 0.8 mmol) were stirred at ~20 °C for 2 h in THF (5 mL) under nitrogen. Formate **5** (89%) was isolated as a colorless liquid by silica gel chromatography with Et_2O as eluent. Found (%): C, 67.74; H, 5.69. $C_{14}H_{14}O_4$. Calculated (%): C, 68.28; H, 5.73; MS, *m/z*: 246.092 [M^+]. M_{calc} = 246.089. IR, ν/cm^{-1}: 1745 and 1735 (C=O); 1615 and 1600 (C=C). ^1H NMR, δ: 1.94 (s, 3 H, CH_3); 4.77 (d, 2 H, CH_2O, ^3J = 6.8 Hz); 5.03 (d, 1 H, =CHH, ^2J = 2.2 Hz); 5.28 (d, 1 H, =CHH, ^2J = 2.2 Hz); 5.83 (t, 1 H, =CH, ^3J = 6.8 Hz); 7.44—7.63 (m, 3 H, Ph); 7.99 (s, 1 H, CHO); 8.10—8.14 (m, 2 H, Ph).

Diethyl 2-((*E*)-4-acetoxy-3-methylpenta-2,4-dien-1-yl)propanedioate (6). Carbonate **3** (1.2 g, 4.2 mmol), diethylmalonate (0.64 mL, 4.2 mmol), and $Pd(PPh_3)_4$ (0.145 g, 0.12 mmol) were stirred at ~20 °C for 16 h in THF (5 mL) under nitrogen. Compound **6** (60%) was isolated as a colorless oil by silica gel chromatography eluting with Et_2O. Found (%): C, 60.35; H, 7.38. $C_{15}H_{22}O_6$. Calculated (%): C, 60.39; H, 7.43%. MS, *m/z*: 298.140 [M^+]. M_{calc} = 298.142. IR, ν/cm^{-1}: 1750 and 1735 (C=O); 1650 and 1615 (C=C). ^1H NMR, δ: 1.20 (t, 6 H, 2 C<u>H</u>$_3$$CH_2O$, ^3J = 7.1 Hz); 1.77 (s, 3 H, CH_3C=); 2.12 (s, 3 H, CH_3CO); 2.64 (t, 2 H, $CHCH_2$, ^3J = 7.5 Hz); 3.31 (t, 1 H, C<u>H</u>$_2$CH, ^3J = 7.5 Hz); 4.11 (q, 4 H, 2 $OCH_2$$CH_3$, ^3J = 7.1 Hz); 4.72 (d, 1 H, =CHH, ^2J = 1.8 Hz); 4.98 (d, 1 H, =CHH, ^2J = 1.8 Hz); 5.53 (t, 1 H, =CH, ^3J = 7.5 Hz).

(*E,E*)-6,6-Diacetyl-3,9-dimethylundeca-1,3,8,10-tetraen-2,10-yl diacetate (7). Carbonate **3** (1.45 g, 5.6 mmol), penta-2,4-dione (0.38 mL, 3.75 mmol), and $Pd(PPh_3)_4$ (0.130 g, 0.11 mmol) were stirred at ~20 °C for 40 h in THF (5 mL) under nitrogen. Compound **7** (62%) was isolated as a colorless oil by silica gel chromatography eluting with an ether—hexane mixture (50 : 50). IR, ν/cm^{-1}: 1755 and 1695 (C=O); 1650 and 1625 (C=C). ^1H NMR, δ: 1.76 (s, 6 H, 2 CH_3=); 2.05 (s, 6 H, 2 CH_3CO); 2.15 (s, 6 H, 2 CH_3CO); 2.63 (d, 4 H, 2 CH_2, ^3J = 7.1 Hz); 4.77 (d, 2 H, 2 =CHH, ^2J = 1.9 Hz); 5.00 (d, 2 H, 2 =CHH, ^2J = 1.9 Hz); 5.20 (t, 2 H, =C<u>H</u>CH_2, ^3J = 7.1 Hz).

Compounds 8 and 9. Carbonate **4** (0.97 g, 2.8 mmol), methyl acetoacetate (0.15 mL, 1.4 mmol), and $Pd(PPh_3)_4$ (0.065 g, 0.06 mmol) were stirred at ~20 °C for 15 h in THF (5 mL) under nitrogen. A mixture of **8** and **9** (92%) was isolated as a colorless liquid by silica gel chromatography eluting with an Et_2O—hexane mixture (50 : 50). The proportions of **8** and **9** were determined by ^1H NMR (**8** : **9** = 2 : 1). IR, ν/cm^{-1}: 1735 and 1715 (C=O); 1650, 1615, and 1600 (C=C).

Methyl (*E*)-2-acetyl-6-benzoyloxy-5-methylhepta-4,6-dienoate (8). ^1H NMR, δ: 1.82 (s, 3 H, CH_3C=); 2.09 (s, 3 H, CH_3CO); 2.58 (t, 2 H, CH_2, ^3J = 7.4 Hz); 3.38 (m, 1 H, $C\underline{H}CH_2$); 3.54 (s, 3 H, CH_3O_2C); 4.85 (d, 1 H, =C$\underline{H}$H, ^2J = 2 Hz), 5.08 (d, 1 H, =CH$\underline{H}$, ^2J = 2 Hz); 5.53 (t, 1 H, =CH, ^3J = 7.4 Hz); 7.38—8.05 (m, 5 H, Ph).

(*E,E*)-6-Acetyl-3,9-dimethyl-6-methoxycarbonylundeca-1,3,8,10-tetraen-2,10-yl dibenzoate (9). ^1H NMR, δ: 1.67 (s, 6 H, 2 CH_3C=); 1.88 (s, 3 H, CH_3CO); 2.51 (d, 4 H, CH_2, ^3J = 7.3 Hz); 3.32 (s, 3 H, $C\underline{H}_3O_2C$); 4.85 (d, 2 H, =CH$\underline{H}$, ^2J = 2 Hz); 5.03 (d, 2 H, 2 =C$\underline{H}$H, ^2J = 2 Hz); 5.36 (t, 2 H, =$CHCH_2$, ^3J = 7.3 Hz); 7.38—8.05 (m, 10 H, Ph).

(*E*)-3-Methyl-5-phenoxypenta-1,3-dien-2-yl benzoate (10). Carbonate **4** (0.8 g, 2.5 mmol), phenol (0.235 g, 2.5 mmol), and $Pd(PPh_3)_4$ (0.06 g, 0.05 mmol) were stirred at ~20 °C for 15 h in THF (5 mL) under nitrogen. Compound **10** (64%) was isolated as a colorless liquid by silica gel chromatography eluting with an hexane—Et_2O mixture (90 : 10). IR, ν/cm^{-1}: 1735 (C=O); 1625 and 1600 (C=C). ^1H NMR, δ: 1.99 (s, 3 H, CH_3C=); 4.66 (d, 2 H, CH_2, ^3J = 6.2 Hz); 5.05 (d, 1 H, =CH$\underline{H}$, ^2J = 1.9 Hz); 5.29 (d, 1 H, =C$\underline{H}$H, ^2J = 1.9 Hz); 6.05 (t, 1 H, ^3J = 6.2 Hz, =$C\underline{H}CH_2$); 6.87—7.32 (m, 5 H, Ph); 7.47—8.15 (m, 5 H, Ph).

3-Methylpenta-1,3-dien-2-yl benzoate (11) and 3-methylpenta-1,4-dien-2-yl benzoate (12). Formate **5** (1 g, 4 mmol) and $Pd(PPh_3)_4$ (0.100 g, 0.09 mmol) were stirred at ~20 °C in THF for 15 h under nitrogen. After evaporation of the solvent and chromatography over silica gel eluting with a hexane—Et_2O mixture (80 : 20) the mixture of **11** and **12** (70 : 30) was collected as a colorless liquid (60%). IR, ν/cm^{-1}: 1750 (C=O); 1620 and 1600 (C=C). ^1H NMR, δ: 1.25 (d, 3 H, $C\underline{H}_3CH$ (**12**), ^3J = 9.2 Hz); 1.70 (dm, 3 H, $C\underline{H}_3CH$= (**11**), ^3J = 7.0 Hz); 1.87 (m, 3 H, $C\underline{H}_3CC$= (**11**)); 3.17 (quint, 1 H, MeC$\underline{H}$ (**12**), ^3J = 7.0 Hz); 4.87 (d, 1 H, =C$\underline{H}$H (**11**), ^2J = 1.5 Hz); 4.93 (s, 2 H, =CH_2 (**12**)); 5.05—5.17 (m, 3 H, =CHH (**11**) + $CH=CH_2$ (**12**)); 5.80—5.92 (m, 2 H, CH_2=CH (**12**) + =C$\underline{H}$Me (**11**)); 7.45—7.63 (m, 6 H, Ph (**11** + **12**)); 8.06—8.17 (m, 4 H, Ph (**11** + **12**)).

References

1. A. J. Clark and P. C. Taylor, in *Comprehensive Organic Functional Group Transformation*, Eds. A. R. Katritzky, O. Meth-Cohin, and C. W. Reeds, Pergamon Press, Cambridge, 1995, 319.
2. J. Tsuji, *Palladium Reagents and Catalysts: Innovations in Organic Synthesis*, J. Wiley and Sons, Chichester, 1995.
3. (a) B. Seiller, C. Bruneau, and P. H. Dixneuf, *Tetrahedron*, 1997, **51**, 13089; (b) B. Cetinkaya, I. Ozdemir, C. Bruneau, and P. H. Dixneuf, *J. Mol. Catal. A: Chem.*, 1997, **118**, L1—L4.
4. C. Bruneau, Z. Kabouche, M. Neveux, B. Seller, and P. H. Dixneuf, *Inorg. Chim. Acta*, 1994, **222**, 155.
5. (a) C. Bruneau and P. H. Dixneuf, *J. Chem. Soc., Chem. Commun.*, 1997, 507; (b) R. Mahé, Y. Sasaki, C. Bruneau, and P. H. Dixneuf, *J. Org. Chem.*, 1989, **54**, 1518.
6. C. Bruneau, M. Neveux, Z. Kabouche, C. Ruppin, and P. H. Dixneuf, *Synlett*, 1991, 755.
7. K. Philippot, D. Devanne, and P. H. Dixneuf, *J. Chem. Soc., Chem. Commun.*, 1990, 199.
8. (a) J. M. Joumier, J. Fournier, C. Bruneau, and P. H. Dixneuf, *J. Chem. Soc., Perkin Trans. 1*, 1991, 3271; (b) J. M. Joumier, C. Bruneau, and P. H. Dixneuf, *J. Chem. Soc., Perkin Trans. 1*, 1993, 1749.
9. M. Neveux, C. Bruneau, and P. H. Dixneuf, *J. Chem. Soc., Perkin Trans. 1*, 1991, 1197.
10. J. M. Joumier, C. Bruneau, and P. H. Dixneuf, *Synlett*, 1992, 453.
11. Y. Hori, T. Mitsudo, and Y. Watanabe, *Tetrahedron Lett.*, 1986, **27**, 5389.
12. C. Goux, P. Lhoste, and D. Sinou, *Synlett*, 1992, 725.
13. (a) R. O. Hutchins and L. Learns, *J. Org. Chem.*, 1982, **47**, 4380; (b) T. Tsuji, I. Shimizu, and I. Minami, *Chem. Lett.*, 1984, 1017; (c) J. Tsuji, *Tetrahedron*, 1986, **42**, 4361; (d) J. Tsuji and T. Mandai, *Synthesis*, 1996, 1.
14. (a) T. Mandai, S. Susuki, T. Murakami, M. Fujita, M. Kawada, and J. Tsuji, *Tetrahedron Lett.*, 1992, **33**, 2987; (b) T. Mandai, T. Matsumoto, and J. Tsuji, *Synlett*, 1993, 113.

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