ELSEVIER

Journal of Molecular Catalysis A: Chemical 116 (1997) 289–296

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

Palladium(0)-catalyzed substitution of allylic substrates in an aqueous-organic medium. Influence of various parameters on the selectivity of the reaction

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Received 30 October 1995; revised 18 March 1996; accepted 20 March 1996

Abstract

The regioselectivity of the reaction of ethyl acetoacetate on allylic carbonate in the presence of a catalyst prepared from $Pd(OAc)_2$ and $P(C_6H_4\text{-}m\text{-}SO_3Na)_3$ (or tppts) is not affected by the ratio $Pd(OAc)_2$/tppts, the nature of the nitrile, the relative amounts of water and nitrile or the temperature of the reaction. Under these conditions the alkylation of various carbonucleophiles having different pK_a gave mainly the monoalkylated products in the case of acyclic carbonucleophiles and dialkylated products in the case of cyclic carbonucleophiles.

Keywords: Palladium; Tppts; Alkylation; Two-phase system

1. Introduction

There is a growing interest in metal catalyzed organic reactions in organic synthesis. One of the most widely used transition metal catalyzed transformation of organic material is probably the palladium catalyzed allylation of carbo- and heteronucleophiles [1–11]. This is probably due to the mildness and very high selectivity of this last reaction. The use of aqueous soluble palladium catalysts emerged only quite recently [12–19]. One of the interest of these catalysts is the very easy separation of the costly and toxic organometallic complex from the organic product(s). Moreover these aqueous palladium catalysts can be used under very mild conditions and sometimes show a different activity or selectivity than the usual soluble catalysts; a very useful application of this methodology is the removal of allyloxycarbonyl protecting group from oxygen and nitrogen [20–22]. In the present paper we report a detailed study on the influence of various parameters on the palladium(0)-catalyzed substitution of allylic substrates in an aqueous-organic medium.

2. Results and discussion

The reaction of ethyl acetoacetate, **2a**, with (*E*)-methyl 2-hexenyl carbonate, **1**, in the presence of a catalytic amount of $Pd(OAc)_2$ associ-

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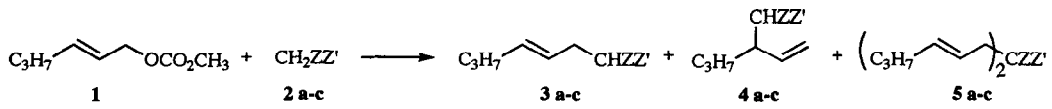
PII S1381-1169(96)00145-8



a: Z = $COCH_3$, Z' = $CO_2C_2H_5$; **b**: Z = Z' = $COCH_3$; **c**: Z = Z' = CO_2CH_3

Scheme 1.

ated with the trisodium salt of the tri(*m*-sulfophenyl)phosphine $P(C_6H_4$-*m*-$SO_3Na)_3$ (or tppts) in a mixture nitrile-water was first studied (Scheme 1). The results summarized in Table 1 show that the regioselectivity of the reaction was not affected by the ratio $Pd(OAc)_2$/tppts, the temperature of the reaction, the ratio water/nitrile or the nature of the nitrile; we always observed the formation of the allylated products ethyl 2-acetyl-4-octenoate, **3a**, and ethyl 2-acetyl-3-propyl-4-pentenoate, **4a**, in a ratio 90 : 10, the compound, **3a**, being a mixture of *E*/*Z* isomers in a ratio 87 : 13.

However the catalytic activity was deeply affected by these different parameters. In a mixture of water/acetonitrile (1 : 1) as the two-phase system at 50°C, the highest activity was obtained for a ratio [tppts]/[$Pd(OAc)_2$] of 9 (entries 1–6); lowering this ratio decreased the conversion of the carbonate. Using this ratio of 9, we noticed that the conversion at 50°C was also dependent of the nature of the nitrile, the highest activity being observed using acetonitrile (entries 5, 14 and 17). This could be related to the partial solubility of the nitrile in water; benzonitrile–water or butyronitrile–water at 50°C is really a two-phase system, and the transfer of the reactants from the organic phase to the aqueous phase for the transformation in the presence of the water-soluble palladium catalyst is probably the limiting step. Conversely, acetonitrile–water at 50°C is not really a two-phase system. This is confirmed by performing the reaction at various temperatures: if low activity was obtained at 25°C using water–acetonitrile as the solvent (entry 7), a complete con-

Table 1
Selectivity in the reaction of ethyl acetoacetate, **2a**, with methyl 2-hexenyl carbonate, **1**, in the presence of $Pd(OAc)_2$/tppts [a]

Entry	Solvent	tppts/$Pd(OAc)_2$	*T*°C	Conv.(%) [b]	**3a**(%) [b]	**4a**(%) [b]
1	CH_3CN/H_2O (5/5)	1/1	50	0		
2	CH_3CN/H_2O (5/5)	4/1	50	0		
3	CH_3CN/H_2O (5/5)	6/1	50	55	89	11
4	CH_3CN/H_2O (5/5)	7.5/1	50	67	90	10
5	CH_3CN/H_2O (5/5)	9/1	50	99	89	11
6	CH_3CN/H_2O (5/5)	12/1	50	99	90	10
7	CH_3CN/H_2O (5/5)	9/1	25	24	90	10
8	CH_3CN/H_2O (5/5)	9/1	75	99	90	10
9	CH_3CN/H_2O (9/1)	9/1	50	71	91	09
10	CH_3CN/H_2O (7/3)	9/1	50	98	90	10
11	CH_3CN/H_2O (3/7)	9/1	50	90	89	11
12	CH_3CN/H_2O (1/9)	9/1	50	81	90	10
13	C_3H_7CN/H_2O (5/5)	9/1	25	09	91	09
14	C_3H_7CN/H_2O (5/5)	9/1	50	47	90	10
15	C_3H_7CN/H_2O (5/5)	9/1	75	98	90	10
16	C_6H_5CN/H_2O (5/5)	9/1	25	06	91	09
17	C_6H_5CN/H_2O (5/5)	9/1	50	60	90	10
18	C_6H_5CN/H_2O (5/5)	9/1	75	90	90	10

[a] Conditions: [carbonate, **1**]/[ethyl acetoacetate]/[$Pd(OAc)_2$] = 25 : 35 : 1; [carbonate, **1**] = 0.5 mol · l^{-1}; 24 h.
[b] Determined by GC.

version of the carbonate was observed at 75°C even using butyronitrile or benzonitrile as the nitrile (entries 15 and 18). In the case of water–acetonitrile we also noticed that the relative amount of water and nitrile had some influence on the activity, the highest activity being obtained with a ratio H_2O/CH_3CN going from 3:7 to 7:3 (entries 5 and 9–12).

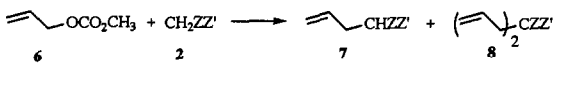
Various compounds bearing active methylene groups and having different pK_a values were also used as nucleophiles in the reaction with allylic carbonates (Table 2). Acetylacetone, **2b** (pK_a = 8.94 in water [23]), reacted with carbonate, **1** (Scheme 1), to give a mixture of monoalkylated acetylacetone, **3b** and **4b**, in a ratio 77:1 with only 2% of the dialkylated product, **5b** (entry 2); we noticed that performing the same reaction in acetonitrile alone gave 29% of the dialkylated product (entry 3). Under the former usual conditions (water/acetonitrile at 50°C) dimethyl malonate, **2c** (pK_a = 13.3 [23]), gave no reaction with carbonate, **1** (entry 4). However, addition of one equivalent of a base such as DBU (entry 5) gave a mixture of monoalkylated products, **3c** and **4c**, in a ratio 67:13 with the formation of approximatively 20% of the alcohol arising from the hydrolysis of the carbonate. The lack of reactivity of dimethyl malonate, **2c**, under the usual conditions compared to ethyl acetoacetate, **2a**, is probably due to its higher pK_a; the presence of water is disadvantageous to the formation of the enolate and the presence of a very strong base such as DBU is needed.

In water/acetonitrile, allyl methyl carbonate, **6**, reacted with ethyl acetoacetate, **2a** (pK_a = 10.5 [23]), leading predominantly to the formation of the product of monoalkylation, **7a**, with a small amount of the dialkylated product, **8a** (88% vs. 12%), contrasting with the result obtained in acetonitrile alone (59% of **7a** and 41% of **8a**) (entries 6 and 7) (Scheme 2). We noticed again in this case that the presence of water decreased the formation of the dialkylated prod-

Table 2
Alkylation of various acyclic carbon nucleophiles in a two-phase system [a]

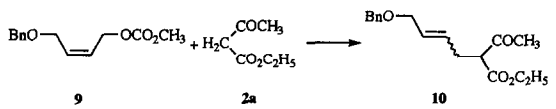
Entry	Carbonate	CH_2ZZ'	Solvent	Products ratio(%) [b]
1	**1**	**2a**	CH_3CN/H_2O (1/1)	**3a** (89%) + **4a** (11%) (*E*/*Z* 87/13)
2	**1**	**2b**	CH_3CN/H_2O (1/1)	**3b** (77%) + **4b** (21%) + **5b** (2%) (*E*/*Z* 78/22)
3	**1**	**2b**	CH_3CN [c]	**3b** (53%) + **4b** (18%) + **5b** (29%) (*E*/*Z* 75/25)
4	**1**	**2c**	CH_3CN/H_2O (1/1)	no reaction
5	**1**	**2c** [d]	CH_3CN	**3c** (67%) + **4c** (13%) [e] (*E*/*Z* 85/15)
6	**6**	**2a**	CH_3CN/H_2O (1/1)	**7a** (88%) + **8a** (12%)
7	**6**	**2a**	CH_3CN [c]	**7a** (59%) + **8a** (41%)
8	**6**	**2c**	CH_3CN/H_2O (1/1)	no reaction
9	**6**	**2d**	CH_3CN/H_2O (1/1)	**7d** (29%) + **8d** (71%)
10	**6**	**2d**	CH_3CN [c]	**7d** (30%) + **8d** (70%)
11	**6**	**2e** [f]	CH_3CN/H_2O (1/1)	**7e** (100%) [g]
12	**6**	**2e** [f]	CH_3CN [c]	**7e** (100%) [h]

[a] Conditions: [carbonate]/[nucleophile]/[palladium]/[tppts] = 25:25:1:9; [carbonate] = 0.5 mol · l^{-1}; 50°C; 24 h.
[b] Determined by GC.
[c] $P(C_6H_5)_3$ was used instead of tppts.
[d] 1 eq. DBU was added.
[e] 20% alcohol was formed.
[f] [carbonate]/[nucleophile] = 35:25.
[g] Conversion 26%, chem. yield 12%.
[h] Conversion 79%, chem. yield 56%.



a: Z = $COCH_3$, Z' = $CO_2C_2H_5$; **b**: Z = Z' = $COCH_3$; **c**: Z = Z' = CO_2CH_3; **d**: Z = Z' = CN; **e**: Z = Z' = $SO_2C_6H_5$

Scheme 2.



Scheme 3.

uct. As expected, no allylation was observed with dimethyl malonate, **2c**, alone as the nucleophile (entry 8).

Dicyanomethane, **2d** (pK_a = 11.2 [23]), gave a mixture of mono- and diallylated products, **7d** (29%) and **8d** (71%), in water–acetonitrile or in acetonitrile alone (entries 9 and 10). Bis(phenylsulfone)methane **2e** (pK_a = 11.2 [23]), gave only the product of monoallylation, **7e**, with, however, a lower yield in the two-phase system (entries 11 and 12).

This difference in reactivity observed with ethyl acetoacetate, **2a**, and dimethyl malonate, **2c**, using a two-phase system instead of an organic phase could be used for the selective alkylation of ethyl acetyl acetate in the presence of dimethyl malonate by methyl allyl carbonate, **6**, (Table 3). The results summarized in Table 3 showed that allylation of a mixture of ethyl acetoacetate, **2a**, and dimethyl malonate, **2c**, in acetonitrile gave mainly the diallylated product, **8a** (entry 1); increasing the amount of carbonate, **6**, lead to the formation of compounds **7c** and **8c** (entry 3). When this reaction was performed in a mixture water-acetonitrile the monoallylated product **7a** was obtained predominantly with some diallylated product **8a**; as expected, only a small amount of products arising from the allylation of dimethyl malonate was observed, whatever the ratio carbonate/carbonucleophile used (entries 2 and 4).

We performed also some experiments using methyl (*Z*) 4-benzyloxy-2-butenyl carbonate, **9**, as the π-allyl precursor (Scheme 3). The results summarized in Table 4 showed that a mixture of (*E*) and (*Z*) isomers, **10**, was obtained in a ratio 85 : 15 in a two-phase system water–nitrile, using $Pd(OAc)_2$ and tppts as the catalyst, whatever the nitrile or the temperature used. Performing the reaction in an organic medium such as acetonitrile using $Pd(OAc)_2$ and $P(C_6H_5)_3$ as the catalyst gave these isomers in a ratio 78 : 22. So even in a two-phase system the π ⇌ σ ⇌ π isomerisation is very fast compared to the rate of attack of the nucleophile on the π-allyl system. The small difference observed in stereoselectivity could be due to a faster rate in the attack of the nucleophile on the π-allyl system in the organic phase.

Finally we used as nucleophiles in this reaction various cyclic carbonucleophiles having very low pK_a (Table 5). The *C*-alkylation of

Table 3
Competitive allylation of **2a** and **2c** by allyl methyl carbonate

Entry	**6**(Eq.)	**2a**(Eq.)	**2c**(Eq.)	Solvent	Products ratio (%)			
					7a	**8a**	**7c**	**8c**
1	3	1	1	CH_3CN [c]	6	84	10	0
2	3	1	1	CH_3CN/H_2O (1/1)	57	34	90	
3	5	1	1	CH_3CN [c]	0	64	15	21
4	5	1	1	CH_3CN/H_2O (1/1)	59	30	0	11

[a] Conditions: [nucleophile]/[palladium]/[tppts] = 25 : 1 : 9; [2] = 0.5 mol · l^{-1}; 50°C; 24 h.
[b] Determined by GC.
[c] $P(C_6H_5)_3$ was used instead of tppts.

Table 4
Alkylation of ethyl acetoacetate, **2a**, by methyl (*Z*) 4-benzyloxy-2-butenyl carbonate, **9** [a]

Entry	Solvent	*T*°C	Conv. (%)	Products ratio (%) [b]	
				10 *E*	**10** *Z*
1	CH_3CN [c]	50	99	78	22
2	H_2O/CH_3CN (1/1)	25	67	85	15
3	H_2O/CH_3CN (1/1)	50	99	85	15
4	H_2O/C_3H_7CN (1/1)	50	99	87	13
5	H_2O/C_6H_5CN (1/1)	50	97	84	16

[a] Conditions: [carbonate **9**]/[nucleophile]/[$Pd(OAc)_2$]/[tppts] = 25 : 35 : 1 : 9; [**9**] = 0.2 mol·l^{-1}; 24 h.
[b] Determined by GC and NMR.
[c] $P(C_6H_5)_3$ was used instead of tppts.

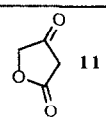
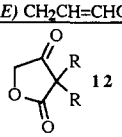
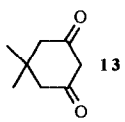
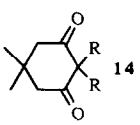
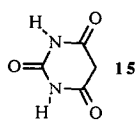
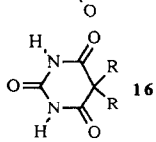
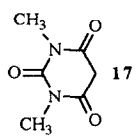
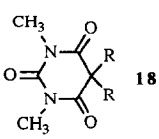
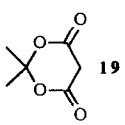
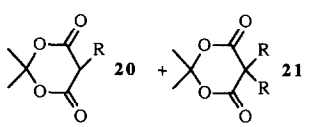
such compounds is sometimes difficult due to strong competitive *O*-alkylation reaction. We expected that the presence of water which was found to inhibit the alkylation of π-allyl systems by nucleophiles such as alcohols or thiols [24] would favor the *C*-alkylation reaction.

Tetronic acid, **11** ($pK_a = 3.76$ [25]) reacted with cinnamyl acetate in the presence of DBU to give only the dialkylated product, **12** (entries 1 and 2), in chemical yields up to 34% identical to the results obtained by Moreno-Mañas et al. [26] using a usual organic system at 65°C.

Under these conditions dimedone, **13** ($pK_a = 5.2$ [23]), gave also only the dialkylated product, **14**, with chemical yield up to 40% (entries 3 and 4). This is in sharp contrast with the literature data where a mixture of monoalkyled and dialkylated product [26] or only monoalkylation [27] was observed.

Barbituric acid, **15** ($pK_a = 4.1$ [28]), and

Table 5
Alkylation of cyclic carbonucleophiles by cinnamyl acetate and ethyl cinnamyl carbonate [a]

Entry	Nucleophile	(*E*) $C_6H_5CH{=}CHCH_2X$	Product (s) R = (*E*) $CH_2CH{=}CHC_6H_5$	Nitrile	Yield (%)
1	 **11**	X = $OCOCH_3$ [b]	 **12**	CH_3CN	34
2		X = $OCOCH_3$ [b]		C_3H_7CN	32
3	 **13**	X = $OCOCH_3$ [b]	 **14**	CH_3CN	30
4		X = $OCOCH_3$ [b]		C_3H_7CN	40
5	 **15**	X = OCO_2CH_3	 **16**	CH_3CN	70
6		X = OCO_2CH_3		C_3H_7CN	69
7	 **17**	X = OCO_2CH_3	 **18**	CH_3CN	62
8		X = OCO_2CH_3		C_3H_7CN	59
9	 **19**	X = $OCOCH_3$ [b]	 **20** + **21**	CH_3CN	17 (**20**) + 32 (**21**)
10		X = $OCOCH_3$ [b]		C_3H_7CN	21 (**20**) + 25 (**21**)

[a] Conditions: [$C_6H_5CH = CHCH_2X$]/[nucleophile]/[$Pd(OAc)_2$]/[tppts] = 35 : 25 : 1 : 6; [nucleophile] = 0.1 mol·l^{-1}; H_2O 5 ml; nitrile 5 ml; 24 h; 50°C.
[b] DBU was added.

1,3-dimethyl barbituric acid, **17** ($pK_a = 4.4$ [28]), gave also exclusively the dialkylated products, **16** and **18** (entries 5–8), with good chemical yields up to 70 and 82%, respectively. Performing the reaction in the case of barbituric acid in tetrahydrofuran [26] gave a mixture of di- and trialkylated products in low chemical yield.

For Meldrum's acid, **19** ($pK_a = 4.83$ [23]), alkylation occurred with chemical yields up to 35%, but with lack of control (relative ratio of **20**:**21** of 35:65 in water/acetonitrile); in an organic phase, a mixture of mono- and dialkylated products, **20** and **21**, was obtained in a relative ratio 22:78 [26], complete dialkylation occurring in the presence of KF on alumina [29].

In conclusion, the regioselectivity of the alkylation of allylic acetate or carbonate by carbonucleophiles in the presence of $Pd(OAc)_2$ and tppts as the catalyst in a nitrile-water medium is independent of the nature of the nitrile, the ratio $Pd(OAc)_2$/tppts or the temperature of the reaction, and is quite similar to those observed in an usual organic medium. However, the selectivity in the formation of mono and dialkylated compounds is very sensitive to the nature of the carbonucleophile and its pK_a; the acyclic carbonucleophiles gave predominantly the monoalkylated product, and the cyclic carbonucleophiles the dialkylated product.

3. Experimental part

All reactions that involved palladium complexes were carried out under nitrogen atmosphere in Schlenk tubes. Column chromatography was performed on silica gel, Merck, grade 60 (230–400 mesh, 60 Å). GC analyses were recorded with a capillary gas chromatography GIRDEL DELSI 330 equipped with a capillary column OV 101 (25 m × 0.32 mm). All compounds were characterized through their ^{1}H- and ^{13}C-NMR spectra, using $CDCl_3$ as the solvent and Me_4Si or chloroform-d_1 as internal standard; carbon multiplicities were obtained from DEPT experiments. The following chemicals were from commercial sources and used as received: $Pd(OAc)_2$, acetonitrile, butyronitrile, benzonitrile, carbonucleophiles **2**, allyl methyl carbonate, cinnamyl acetate, (*E*)-2-hexen-1-ol, DBU or diazabicyclo[5,4,0]undec-7-ene, (*Z*)-4-benzyloxy-2-buten-1-ol, tetronic acid **11**, dimedone **13**, barbituric acid **15**, 1,3-dimethylbarbituric acid **17**, Meldrum's acid **19** and PPh_3 were from commercial sources. The alcohols were converted to the corresponding carbonates in good yields using standard procedures. The compounds **3a** and **4a** [22,30], **3b** and **4b** [31], **7a** and **8a** [30,32], **7d** [32], **7e** [32], **12** [29], **16** [29], **20** and **21** [29] were already described.

General procedure for the palladium-catalyzed alkylation of carbonucleophiles. A mixture of $Pd(OAc)_2$ (4 mol%) and tppts (36 mol%) was stirred in H_2O (2.5 ml) for 1 h. The allylic compound and the nucleophile, and eventually DBU, in 2.5 ml of nitrile was then added and the reaction mixture was stirred at the desired temperature. The solvent was evaporated and the residue was purified by column chromatography on silica gel to give the desired product(s).

(*E*)- and (*Z*)-methyl 2-methoxycarbonyl-4-octenoate, 3c, and methyl 3-vinyl-2-methoxycarbonylhexanoate, 4c. These compounds were characterized in the mixture. ^{1}H-NMR (200 MHz): δ 0.86 (t, 3 H, $J = 7.4$ Hz, CH_3), 1.25–1.40 (m, CH_3CH_2 and $CH_2CH<$ of **4**), 1.90–1.97 (m, $CH_2CH=$ of **3** and $CHCH=$ of **4**), 2.60 (dd, $J = 6.7$ and 6.7 Hz, $CH_2CH<$ of **3c**), 3.38 (d, $J = 7.4$ Hz, $-CH<$ of **4c**), 3.42 (t, $J = 7.7$ Hz, $-CH<$ of **3c**), 3.70 (s, 6 H, OCH_3), 5.30–5.56 (m, $-CH=$ and $=CH_2$). ^{13}C-NMR (50 MHz): for *(E)* **3c** δ 13.75 (CH_3CH_2), 22.45 (CH_3CH_2), 31.99 ($CH_2CH<$), 34.55 ($-CH_2CH=$), 52.07 ($-CH<$), 52.40 (OCH_3), 125.32 ($-CH=$), 133.98 ($-CH=$), 169.98 (CO_2); for *(Z)* **3c** δ 13.75 (CH_3CH_2), 22.67 (CH_3CH_2), 26.82 ($CH_2CH<$), 29.25 ($-CH_2CH=$), 51.81 ($-CH<$), 52.40 (OCH_3), 124.58 ($-CH=$), 133.19 ($-CH=$),

169.98 (CO_2); for **4c** δ 13.80 (CH_3CH_2), 20.17 (CH_3CH_2), 34.49 ($CH_2CH<$), 44.04 (–$CHCH=$), 52.40 (OCH_3), 56.95 (–$CHCO_2CH_3$) 117.37 ($=CH_2$), 138.14 (–CH=), 168.82 (CO_2).

(*E*)- and (*Z*)-ethyl 2-acetyl-6-benzyloxy-4-hexenoate, 10. Compounds *Z* and *E* were characterized in the mixture. ^{1}H-NMR (200 MHz): δ 1.26 (t, 3 H, $J = 7.1$ Hz, CH_2CH_3), 2.23 (s, 3 H, $COCH_3$), 2.59 (dd, 2 H, $J = 7.5$ and 7.3 Hz, $CH_2CH<$), 3.50 (t, 1 H, $J = 7.5$ Hz, –CH <), 3.94 (d, 2 H, $J = 4.2$ Hz, $OCH_2CH=$), 4.20 (q, 2 H, $J = 7.1$ Hz, CH_2CH_3), 4.47 (s, 2 H, $CH_2C_6H_5$ of *E* isomer), 4.50 (s, 2 H, $CH_2C_6H_5$ of *Z* isomer), 5.64–5.74 (m, 2 H, –CH=), 7.20–7.30 (m, 5 H, C_6H_5). ^{13}C-NMR (50 MHz): δ *E* isomer 14.10 (CH_3), 29.09 ($COCH_3$), 30.78 ($CH_2CH<$), 59.35 (–CH <), 61.45 (CH_2CH_3), 70.29 ($OCH_2CH=$), 71.97 ($CH_2C_6H_5$), 126.27–138.27 (C_6H_5, =CH–), 169.18 (CO_2), 202.33 (CO); *Z* isomer 14.10 (CH_3), 26.32 ($CH_2CH<$), 29.23 ($COCH_3$), 59.26 (–CH <), 61.35 (CH_2CH_3), 65.18 ($OCH_2CH=$), 72.39 ($CH_2C_6H_5$), 126.27–138.27 (C_6H_5, =CH–), 169.18 (CO_2), 202.33 (CO)

2,2-Di-(*E*)-cinnamyl-5,5-dimethylcyclohexane-1,3-dione, 14. Yellow solid. M.p. 149°C. ^{1}H-NMR (200 MHz): δ 0.95 (s, 6 H, CH_3), 2.57 (s, 4 H, CH_2CO), 2.70 (d, 4 H, $J = 7.5$ Hz, $CH_2CH=$), 6.02 (dt, 2 H, $J = 15.8$ and 7.5 Hz, $CH_2CH=$), 6.43 (d, 2 H, $J = 15.8$ Hz, $=CHC_6H_5$), 7.10–7.30 (m, 10 H, C_6H_5). ^{13}C-NMR (50 MHz): δ 28.54 (CH_3), 38.20 (C-4, C-6), 52.07 ($CH_2CH=$), 68.42 (C-5), 123.82 ($CH_2CH=$), 126.15, 127.35, 128.43 and 136.89 (C_6H_5), 134.35 ($=CHC_6H_5$), 208.79 (C-1, C-3). Anal. Calcd. for $C_{26}H_{28}O_2$: C, 83.83; H, 7.58. Found: C, 83.36; H, 7.63.

1,3-Dimethyl-5,5-di-(*E*)-cinnamyl-pyrimidine-2,4,6-trione, 18. Oil. ^{1}H-NMR (200 MHz): δ 2.91 (d, 4 H, $J = 7.7$ Hz, $CH_2CH=$), 3.25 (s, 6 H, CH_3), 5.92 (dt, 2 H, $J = 15.7$ and 7.7 Hz, $CH_2CH=$), 6.48 (d, 2 H, $J = 15.7$ Hz, $=CHC_6H_5$), 7.20–7.30 (m, 10 H, C_6H_5). ^{13}C-NMR (50 MHz): δ 28.26 (CH_3), 42.08 (CH_2), 57.63 (C-5), 121.56 ($CH_2CH=$), 126.15, 127.70, 128.43 and 136.29 (C_6H_5), 135.35 ($=CHC_6H_5$), 150.67 (C-4, C-6), 170.62 (C-2). Anal. Calcd. for $C_{24}H_{24}N_2O_3$: C, 74.20; H, 6.23. Found: C, 74.03; H, 6.12.

Acknowledgements

We thank the MESR for a fellowship (to S.S.).

References

[1] B.M. Trost, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 8, Pergamon Press, New York, 1982, p. 799.
[2] B.M. Trost, Acc. Chem. Res., 13 (1980) 385.
[3] B.M. Trost, Chemtracts-Organic Chemistry, 1 (1988) 415.
[4] B.M. Trost, Angew. Chem. Int. Ed. Engl., 28 (1989) 1173.
[5] S.A. Goldeski, in B.M. Trost (Ed.), Comprehensive Organic Synthesis, Vol. 4, Pergamon Press, Oxford, 1991, p. 585.
[6] J. Tsuji, Organic Synthesis with Palladium Compounds, Springer-Verlag, Berlin, 1980.
[7] J. Tsuji and I. Minami, Acc. Chem. Res., 20 (1987) 140.
[8] J. Tsuji, Tetrahedron, 42 (1986) 4361.
[9] R.F. Heck, Palladium Reagents in Organic Synthesis, Academic Press, London, 1985.
[10] G. Consiglio and R.M. Waymouth, Chem. Rev., 89 (1989) 257.
[11] C.G. Frost, J. Howarth and J.M.J. Williams, Tetrahedron: Asymmetry, 3 (1992) 1089.
[12] N.A. Bumagin, P.G. More and I.P. Beletskaya, J. Organomet. Chem., 371 (1989) 397.
[13] A.L. Casalnuovo and J.C. Calabrese, J. Am. Chem. Soc., 112 (1990) 4324.
[14] M. Safi and D. Sinou, Tetrahedron Lett., 32 (1991) 2025.
[15] J. P. Genêt, E. Blart and M. Savignac, Synlett, (1992) 715.
[16] E. Blart, J. P. Genêt, M. Safi, M. Savignac and D. Sinou, Tetrahedron, 50 (1994) 505.
[17] S. Sigismondi, D. Sinou, M. Pérez, M. Moreno-Mañas, R. Pleixats and M. Villaroya, Tetrahedron Lett., 35 (1994) 7085.
[18] J. P. Genêt, A. Linquist, E. Blart, V. Mouriès, M. Savignac and M. Vaultier, Tetrahedron Lett., 36 (1995) 1443.
[19] A.I. Roshchin, N.A. Bumagin and I.P. Beletskaya, Tetrahedron Lett., 36 (1995) 125.
[20] J.P. Genêt, E. Blart, M. Savignac, J.M. Paris and J.M. Bernard, Tetrahedron Lett., 34 (1993) 4189.
[21] S. Lemaire-Audoire, M. Savignac, E. Blart, G. Pourcelot, J.P. Genêt and J.M. Bernard, Tetrahedron Lett., 35 (1994) 8783.
[22] J. P. Genêt, E. Blart, M. Savignac, S. Lemeune, S. Lemaire-

Audoire, J. M. Paris and J. M. Bernard, Tetrahedron, 50 (1994) 497.
[23] O. A. Reutov, I. P. Beletskaya, K. P. Butin, CH-acids, Pergamon Press, Oxford, 1978.
[24] C. Goux, M. Massacret, P. Lhoste and D. Sinou, Organometallics, 14, (1995) 4595.
[25] W.D. Kumler, J. Am. Chem. Soc., 60 (1938) 859.
[26] M. Prat, M. Moreno-Mañas and J. Ribas, Tetrahedron, 44 (1988) 7205.
[27] B.M. Trost and D.M.T. Chan, J. Am. Chem. Soc., 101 (1979) 6432.
[28] J.T. Bojarski, J.L. Mokrosz, H.J. Barton, M.H. Paluchowska, Adv. Heterocycl. Chem., 38 (1985) 229.
[29] D. Ferroud, J.P. Genêt and J. Muzart, Tetrahedron Lett., 29 (1984) 4379.
[30] S.W. Zhang, T. Mitsudo, T. Kondo and Y. Watanabe and X. Tao, J. Organomet. Chem., 450 (1993) 197.
[31] M. Moreno-Mañas and A. Trius, Tetrahedron, 37 (1981) 3009.
[32] X. Lu, X. Jiang and X. Tao, J. Organomet. Chem., 344 (1988) 109.