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Dihydromyrcenol carbonylation catalyzed by palladium–tin precursors: selectivity of the reaction drawn by the experimental conditions and the co-reactants

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Abstract

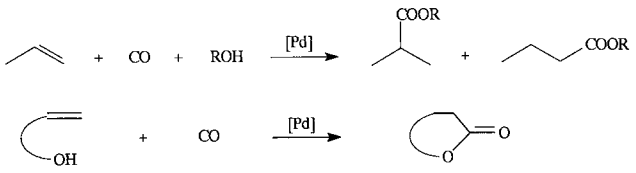
The methoxycarbonylation of dihydromyrcenol **1** has been carried out in the presence of the catalytic system $[PdCl_2(PPh_3)_2]$–$SnCl_2{\cdot}2H_2O$–$2PPh_3$. This study shows that it is possible to reduce the amounts of isomerization of the terminal double bond and the dehydration side-reaction of the tertiary alcoholic function. According to the experimental conditions ($P_{CO} = 40$ or 100 bar, concentration of methanol, experiment duration, temperature) it is possible to orient the reaction towards the three 'linear' esters **4**, **5**, **6**, and lactone **8**. This latter product has been exclusively obtained when the acidity of the medium is controlled. Nevertheless it is more difficult to obtain one ester from each others.

Keywords: Carbonylation; Hydroesterification; Lactone; Palladium; Terpenes

1. Introduction

The alkoxycarbonylation of alkenes is an elegant way to produce directly esters or related derivatives like lactones [1] (Scheme 1).

Usually palladium complexes catalyze this reaction under medium-pressure conditions, and it has been shown in the early studies that tin dichloride plays a promoting role in this reaction [2]. The exact role of $SnCl_2$ is not clear, since, if we transpose the chemistry of the related platinum complexes where Pt–$SnCl_3$ is formed from a Pt–Cl bond, it should enter the coordination sphere of palladium to become a ligand. However, it can also promote the migratory insertion of CO into the alkyl bond due to its Lewis acidity [3]. Generally the starting material is $[PdCl_2(PPh_3)_2]$ which is of an easy access; in the presence of $SnCl_2$, it should give $[PdCl(SnCl_3)(PPh_3)_2]$. Indeed, it is analogous to $[PtCl(SnCl_3)(PPh_3)_2]$ which has been isolated and fully characterized [3a,4]. Moreover, $[PdCl(SnCl_3)(PPh_3)_2]$ has been observed in solution by NMR and the tin–phosphorus coupling constant measured [5]. Other phosphine or diphosphine ligands have also been used [6].



Scheme 1.

During several years, the mechanism of catalysis has been controversial due to the possibility of a 'Pd–H' route in competition with a Pd–COOMe carbomethoxy route [7]. Several indirect evidences support the hydrido route [8]. Particularly, during our studies on terpenes we have intercepted traces of an unsaturated cyclopentenone; it results in a first step from a CH allylic cleavage in isolimonene by the palladium precursor [9].

Terpenes represent an interesting pool as substrates since from the C10 framework and the various unsaturations it contains their functionalization is possible. Thus, the access to oxygenated products is of interest due to their potential activity in perfumery [10]. We

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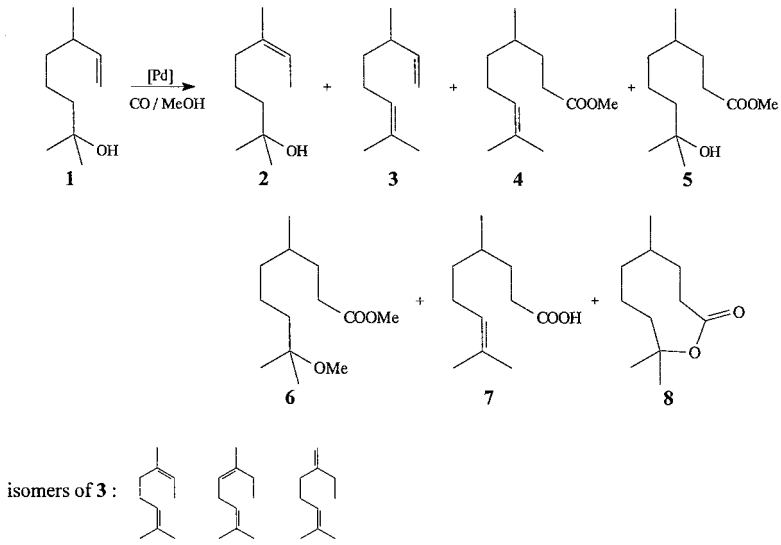
Table 1
Reactions of alkoxycarbonylation of dihydromyrcenol **1**: [**1**]/[$PdCl_2(PPh_3)_2$] = 50, methanol = 50 mmol

Run	T (°C)	Time (h)	Conversion (%)	Yield (%)							Selectivity of **4**–**8** (%)
				2	**3**	**4**	**5**	**6**	**7**	**8**	
1	72	16	87	15	11	19	19	14	7	2	70
2	82	16	100	–	11	32	5	11	30	11	89
3	92	16	100	–	10	41	3	3	34	9	90
4	72	40	100	–	10	42	10	4	30	4	90
5 [a]	80	16	100	–	4	43	6	4	40	3	96
6 [b]	72	16	52	10	2	3	8	27 (52) [c]	2	–	77
7 [b]	72	40	99	1 [d]	7	13	39	24	1 [d]	14	90

Conditions: [$PdCl_2(PPh_3)_2$] = 1 mmol, excess of phosphine = 2 mmol, $SnCl_2 \cdot 2H_2O$ = 2.5 mmol, toluene = 25 ml, P_{CO} = 40 bar.
[a] P_{CO} = 100 bar.
[b] methanol = 300 mmol.
[c] Selectivity (%).
[d] Peak observed by chromatography and considered to be 1% as the method limit.



Scheme 2.

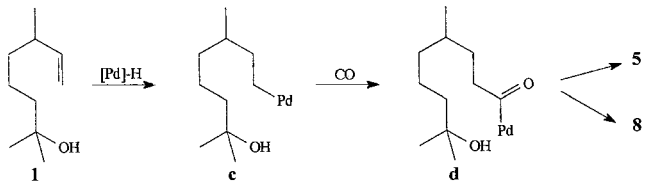
were interested in the methoxycarbonylation of dihydromyrcenol, which contains a terminal C=C bond and a tertiary alcohol function as well, with the aim to induce the formation of a lactone by a tandem reaction. This paper deals with the examination of the main reaction parameters to drive the carbonylation of this substrate.

2. Results and discussion

2.1. General test

The catalytic system introduced in the autoclave is [$PdCl_2(PPh_3)_2$] and $SnCl_2 \cdot 2H_2O$, in the presence of an excess of two equivalents of triphenylphosphine in order to maintain a molar [PPh_3]/[Pd] ratio of 4. A series of experiments has been done in toluene, as usual [9], with 50 equivalents of methanol, for fifty equivalents of dihydromyrcenol. The CO pressure was 40 bar, and the temperature was ranging between 72 and 92 °C, for 16 h. Table 1 displays the general runs and shows that the total selectivity in carbonylated products (last column) varies between 70 and 90%, but can reach 96% at 100 bar (run 5). Scheme 2 shows the various products which have been formed during this studies. It can be mentioned that the addition of anhydrous $SnCl_2$ provides the same results. However if [$PdCl_2(PPh_3)_2$] is introduced in the absence of tin chloride, we checked that the yields were dramatically reduced since the conversion was lowered to 20%.

Significant amounts of compounds **3** and/or **2** were systematically found after each experiment: **2** results from an isomerisation reaction which classically in-



Scheme 3.

volves the coordination of **1** to a palladium hydride species, followed by a β-H elimination. Only isomer **2** has been detected by GC–MS and ^{1}H-NMR. Compound **3** has been formed by dehydration of **1**, presumably due to the presence of an acidic medium produced by the loss of HCl when the palladium hydride species was produced [9]. GC–MS experiments have shown that several isomers were formed: as the methylpropenyl fragment was observed, only the terminal carbon–carbon double bond should have migrated towards internal positions; only isomer **3** is represented. This isomer was the starting material for the hydroesterification or hydroxycarbonylation giving rise to the unsaturated ester **4** and acid **7**, respectively. The ester **6** resulted presumably directly from **4** or **3**, depending on the relative order of electophilic addition of methanol and carbonylation, however, the methylether of **1** has not been detected. Nevertheless, formation of **6** from **5** with methanol in acid medium could be envisioned.

When the temperature was raised from 72 to 82 and 92 °C, no more compound **2** was found in the solution, because the dehydration process was faster (the yields of **4** and **7** increased) and some internal isomers of **3** were still produced from **2**. It is important to underline that only the isomer of **3** as represented on Scheme 2 reacted to produce **4**, **6** and **7**, as terminal esters or acid and all others branched esters have not been detected. Similarly, reduced amounts of **2**, and even **4** can result from an increase in the reaction time (run 4) or in the CO pressure (100 bar, run 5); parallel greater quantities of **7**, and in a lesser extent of **4** can be noted.

Direct hydroesterification of **1** produced **5**, which can give **4** by dehydration. Lactone **8** resulted from the direct cyclization of the acyl intermediate **d** [8b,9b,9c,11,12], which concurrently produced **5** when methanol reacted instead of the inner alcohol function (Scheme 3).

The effects of a methanol excess have also been investigated. Runs 6 and 7 of Table 1 are related to a molar ratio [MeOH]/[**1**] of 6. The rate of the reaction decreased significantly as the conversion are 87% for run 1, and 52% for run 6. The main product obtained in this latter run was compound **6** with a 52% selectivity; poor yields in the other products can be noted. Increasing the time to 40 h (run 7) resulted in profound modifications in the various selectivities. The conversion was almost complete and 39% of compound **5** were obtained. Simultaneously, 14% of lactone **8** were produced. In our opinion, the higher concentration of methanol induced a faster neutralization of HCl. It could occur through the formation of CH_3Cl, which was removed in the gas phase when the 40 bar of CO were depressurized, and thus not detected, or it could be associated with methanol through hydrogen bonds. In the absence of an acidic medium, products **5** and **8** were favored.

2.2. Esters *4*, *5*, and *6*

In order to direct the carbonylation reaction towards the esters, we have increased the concentration in methanol. The results are displayed in Tables 2 and 3. In each case, the molar [substrate]/[Pd] ratio has been increased to 100; Table 2 refers to a [methanol]/[Pd] ratio of 100, whereas Table 3 concerns a ratio of 300.

In general, the three esters were obtained simultaneously most of the time. Run 8 shows that they can be produced roughly in the absence of the other carbonylated products; the presence of large amounts of isomer **2** reduced the selectivity in esters to 66%. It is worth mentioning that the selectivity in the ether–ester **6**

Table 2
Reactions of alkoxycarbonylation of dihydromyrcenol **1**: [**1**]/[$PdCl_2(PPh_3)_2$] = 100, methanol = 100 mmol

Run	T (°C)	Time (h)	Conversion (%)	Yield (%)							Selectivity of **4**–**8** (%)
				2	**3**	**4**	**5**	**6**	**7**	**8**	
8	72	16	39	12 (34) [a]	1 [b]	2	4	18 (46) [a]	1 [b]	1 [b]	66
9	84	16	100	–	12	28	24	20	12	4	88
10	72	40	96	3	8	20 (21) [a]	24 (25) [a]	27 (28) [a]	12	2	89
11 [c]	80	16	100	–	13	23	21	24	12	7	87

Conditions: [$PdCl_2(PPh_3)_2$] = 1 mmol, excess of phosphine = 2 mmol, $SnCl_2{\cdot}2H_2O$ = 2.5 mmol, toluene = 25 ml, P_{CO} = 40 bar.
[a] Selectivity (%).
[b] Peak observed by chromatography and considered to be 1% as the method limit.
[c] P_{CO} = 100 bar.

Table 3
Reactions of alkoxycarbonylation of dihydromyrcenol **1**: [**1**]/[$PdCl_2(PPh_3)_2$] = 100, methanol = 300 mmol

Run	T (°C)	Time (h)	Conversion (%)	Yield (%)							Selectivity of **4–8** (%)
				2	**3**	**4**	**5**	**6**	**7**	**8**	
12	72	16	43	14 (37) [a]	1 [b]	1 [b]	3	13	–	11	63
13	66	40	35	8	1 [b]	–	23 (66) [a]	3	–	–	74
14	72	40	74	19	3	7	18 (24) [a]	22 (30) [a]	1 [b]	4	70
15	84	40	100	–	8	30	39	13	8	2	92
16	92	40	100	–	16	31	11	36	5	1 [b]	84
17 [c]	80	16	88	9	12	12	25 (28) [a]	27 (31) [a]	1 [b]	2	76

Conditions: [$PdCl_2(PPh_3)_2$] = 1 mmol, excess of phosphine = 2 mmol, $SnCl_2 \cdot 2H_2O$ = 2.5 mmol, toluene = 25 ml, P_{CO} = 40 bar.
[a] Selectivity (%).
[b] Peak observed by chromatography and considered to be 1% as the method limit.
[c] P_{CO} = 100 bar.

shows the higher value of all our experiments and reached 46%.

From run 13, we can conclude that the high concentration in methanol together with the relatively low temperature adopted for the experiment allowed a good selectivity (66%) in the expected ester **5**. That means that the activation energy for the transformation **d** → **5** is lower than **d** → **8**.

However, the increase of the temperature had dramatic effects. From run 16, it appears that extensive dehydration has taken place. Thus, even if an excess of methanol reduced the negative effect of HCl, the presence of an acidic medium at the early stage of the reaction induced the formation of **3**, and thus **4** and **6**, which results from the methoxylation of **4**. Due to the relatively important concentration of methanol, few quantities of acid **7** were formed.

The general trend for higher pressures (runs 5, 11 and 17) is, as expected, an increase in the proportion of carbonylated products. For instance, in run 11, comparable quantities (ca. 23%) of **4**, **5**, or **6** were obtained. Of course, in the presence of a methanol excess, ether **6** was a little bit more abundant.

Longer reaction times induced higher conversion rates. When a 100% yield was reached, isomer **2** was no more present, because it can give the dehydration product **3**, or after transfer of hydride from a Pd–H species the back isomerization, although it is slow, towards the terminal C–C double bond. This phenomenon is induced by the steric hindrance of the coordination sphere of palladium and the bulkiness of PPh_3 is important.

2.3. Unsaturated acid 7 and lactone 8

As already described in Section 2.1, abundant quantities of ester **4** and acid **7** can be produced in the presence of few amounts of methanol and at high pressure (run 5), or at higher temperature (run 3), or for longer reaction times (run 4). Of course, if methanol is not introduced, the production of the acid **7** or lactone **8** would be favored. At 100 bar and for 16 h ([**1**]/[Pd] = 100) we obtained 92% of **7** for a 100% conversion rate, absence of **8** and 8% of isomer **3** [12]. We never observed the saturated acid, which would correspond to the hydroxycarbonylation of **1**.

The experiments carried out with an excess of methanol revealed the formation of some significant amounts of lactone **8**, presumably due to some neutralization of HCl. In order to promote the cyclization of species **d**, and to have a great selectivity in **8**, we introduced molecular sieves to remove HCl as soon as it was formed, and the amounts of water co-produced as well. We have previously reported [12] that such an addition allowed to reach a selectivity in **8** as high as 98%. Thus, at 40 bar and for a conversion of 60% after 40 h, only traces of isomer **3** were detected.

In conclusion, carbonylation of dihydromyrcenol **1**, catalyzed by [$PdCl_2(PPh_3)_2$]/$SnCl_2 \cdot 2H_2O$/2PPh_3, occurred readily under medium pressure conditions to give three esters, one acid and a lactone. Modifications of the experimental conditions allowed us to direct the reaction towards one carbonylated product. However, the main problem which appeared was the acidity of the medium due to the formation of HCl when the palladium hydride species was initiated. The addition of molecular sieves trapped this acidity and directed the reaction to the lactone **8**. An excess of methanol induced the formation of the three esters, although it was difficult to privilege one of them. All the observations we have done in this study are summarized in Scheme 4.

3. Experimental

3.1. General

The ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were recorded with $CDCl_3$ solutions containing TMS as internal stan-

dard on a Bruker AM250 spectrometer operating at 250.13, 62.90 and 101.26 MHz, respectively. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant in Hz (J), integration, and assignation. IR spectra were obtained on a Perkin–Elmer 1710 spectrometer; absorptions are reported in cm^{-1}. Analytical GC was carried out on a Carlo Erba MFC 500 apparatus equipped with a Econo-Cap FFAP (30 m; 0.53 mm; 1.2 μm) capillary column and a flame ionization detector. Products were identified by GC–MS on a Perkin–Elmer QMass 910 Mass Spectrometer (MS) with ionization voltage of 70 eV, with a Crompack CP WAX 52 CB (50 m; 0.32 mm; 0.2 μm) polar column. Elemental analyses were performed by the Analytic Laboratory of ENSIACET. Column chromatography was performed with SiO_2 (Merck).

3.2. Materials

$[PdCl_2(PPh_3)_2]$ was prepared according to the literature [13], (yield 95%), $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ_p 23.47 (s), IR $\nu = 1481$, 1436, 1099, 746, 693. Solvents with high purity (toluene, methanol) have been used as received, as well as dihydromyrcenol (DRT SA), $SnCl_2$ (Aldrich > 99%), $SnCl_2{\cdot}2H_2O$ (Prolabo 98%), triphenylphosphine (Aldrich 99%).

3.3. Typical procedure

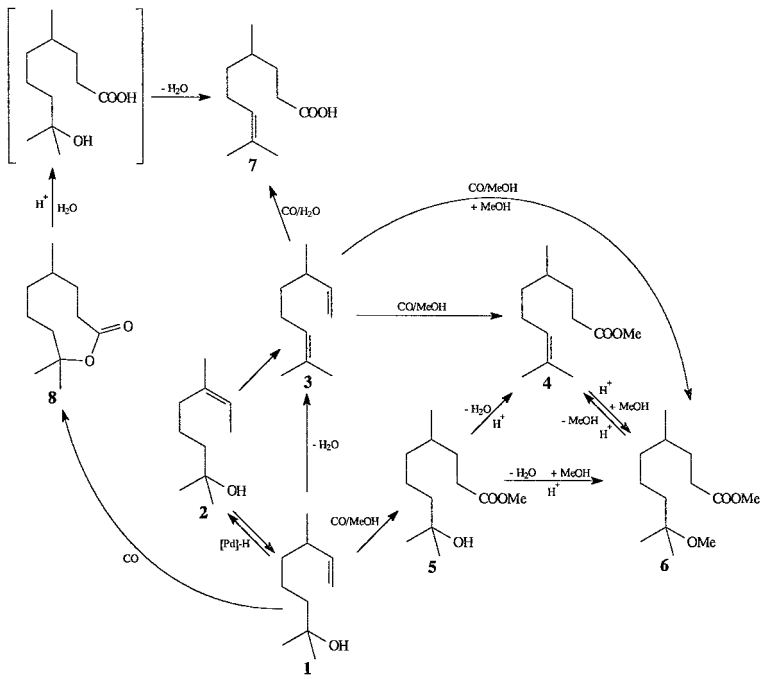
A mixture of 0.702 g (1 mmol) of dichlorobis(triphenylphosphine)palladium(II), 0.474 g (2.5 mmol) of hydrated tin(II) chloride and 0.524 g (2 mmol) of triphenylphosphine was introduced into a 250 ml stainless steel autoclave with mechanical stirring. A dinitrogen-saturated mixture of 7.814 g of dihydromyrcenol (50 mmol) and 1.602 g of methanol (50 mmol) in 25 ml toluene was introduced into the evacuated autoclave by aspiration. It was heated to 72 °C under 40 bar of carbon monoxide at constant pressure. After 16 h, the autoclave was cooled and then slowly depressurized. The yellow–orange reaction mixture was analyzed by gas chromatography.

After the catalytic reaction, the organometallic compounds and the phosphine excess were separated from the crude solution by adding CCl_4. The deeply colored oily layer was decanted. After concentration by rotary evaporation, the oily residue was purified by column chromatography on silica gel.

3.4. Characterization of the products

3.4.1. Methyl 4,8-dimethylnon-7-enoate (4)

Incolore oil; (eluent: heptane–dichloromethane–ethyl acetate = 75/12.5/12.5); ^{1}H-NMR ($CDCl_3$): δ 5.01 (t, n.d., 1H, H7), 3.58 (s, 3H, CH_3 12), 2.25 (m, 2H, H5), 1.88 (m, 1H, H4), 1.60 (s, 3H, CH_3 9), 1.52 (s, 3H,



Scheme 4.

CH_3 10), 1.34–0.82 (m, 6H, H2, H3 and H6), 0.80 (d, $J = 6$ Hz, 3H, CH_3 11); ^{13}C-NMR ($CDCl_3$): δ 174.4 (C1), 131.1 (C7), 124.6 (C8), 51.3 (C12), 36.7 (C5), 32.0, 31.9 and 31.8 (C2, C3 and C4), 25.6 and 25.4 (C9 and C10), 19.1 (C11), 17.5 (C6); IR (neat): 1712 (C=O); MS, m/z (relative intensity, %): 199 (1), 198 [M^+, 2], 183 (11), 74 (100), 69 (100), 41 (51). Anal. Calc. for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18; O, 16.14. Found: C, 71.85; H, 11.80; O, 16.44%.

*3.4.2. Methyl 4,8-dimethyl-8-hydroxynonanoate (**5**)*

Incolore oil; (eluent: heptane–dichloromethane–ethyl acetate = 90/5/5); ^{1}H-NMR ($CDCl_3$): δ 3.53 (s, 3H, CH_3 12), 2.18 (m, 2H, H5), 2.09 (m, 1H, H4), 1.53 (m, 2H, H3), 1.28 (m, 4H, H6 and H7), 1.14 (t, n.d., 2H, H2), 1.07 (s, 6H, CH_3 9 and CH_3 10), 0.75 (d, $J = 6.1$ Hz, 3H, CH_3 11); ^{13}C-NMR ($CDCl_3$): δ 174.2 (C1), 70.4 (C8), 51.2 (C12), 43.8 (C7), 37.0 (C5), 32.1, 31.6 and 31.5 (C2, C3 and C4), 28.9 and 28.8 (C9 and C10), 21.4 (C11), 19.0 (C6); IR (neat): 1729 (C=O); MS, m/z (relative intensity, %): 217 [M^+ 1, 5], 201 (12), 199 (100), 87 (100), 74 (14), 59 (100), 43 (81). Anal. Calc. for $C_{12}H_{24}O_3$: C, 66.63; H, 11.18; O, 22.19. Found: C, 66.29; H, 10.78; O, 22.37%.

*3.4.3. Methyl 4,8-dimethyl-8-methoxynonanoate (**6**)*

Orange oil; (eluent: heptane–dichloromethane–ethyl acetate = 90/5/5); ^{1}H-NMR ($CDCl_3$): δ 3.59 (s, 3H, CH_3 12), 3.10 (s, 3H, CH_3 13), 2.25 (m, 1H, H4), 1.63–1.31 (m, 10H, H2, H3, H5, H6 and H7), 1.06 (s, 6H, CH_3 9 and CH_3 10), 0.81 (d, $J = 6.1$ Hz, 3H, CH_3 11); ^{13}C-NMR ($CDCl_3$): δ 174.2 (C1), 74.3 (C8), 51.2 (C12), 48.8 (C13), 40.0 (C7), 37.1 (C5), 31.7 and 31.6 (C4, C3 and C2), 24.7 (C9 and C10), 21.0 (C11), 19.0 (C6); IR (neat): 1730 (C=O); MS, m/z (relative intensity, %): 231 [M^+ 1,1], 199 (1), 74 (11), 73 (100), 41 (41). Anal. Calc. for $C_{13}H_{26}O_3$: C, 67.79; H, 11.38; O, 20.84. Found: C, 67.57; H, 10.87; O, 19.46%.

*3.4.4. Acid 4,8-dimethylnon-7-enoique (**7**)*

Incolore oil; (eluent: heptane–dichloromethane–ethyl acetate = 90/5/5); ^{1}H-NMR ($CDCl_3$): δ 10.79 (m, 1H, OH), 5.05 (t, $J = 6$ Hz, 1H, H7), 2.31 (m, 2H, H5), 1.95 (m, 1H, H4), 1.64 (s, 3H, CH_3 9), 1.57 (s, 3H, CH_3 10), 1.5-1.1 (m, 6H, H2, H3 and H6), 0.86 (d, $J = 6.1$ Hz, 3H, CH_3 11); ^{13}C-NMR ($CDCl_3$): δ 180.8 (C1), 131.1 (C7), 124.4 (C8), 36.5 (C5), 31.7 and 31.2 (C2, C3 and C4), 25.5 and 25.2 (C9 and C10), 19.0 (C11), 14.5 (C6); IR (neat): 1709 (C=O); MS, m/z (relative intensity, %): 185 [M + 1, 2], 124 (3), 69 (100), 41 (99). Anal. Calc. for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94; O, 17.36. Found: C, 71.91; H, 11.40; O, 16.69%.

*3.4.5. 4,8,8-trimethyloctano-8-lactone (**8**)*

Incolore oil; (eluent: heptane–dichloromethane–ethyl acetate = 75/15/10); ^{1}H-NMR ($CDCl_3$): δ 2.16 (m, 2H, H7), 1.91 (m, 1H, H4), 1.63–1.49 (m, 6H, H3, H5 and H6), 1.35 (s, 6H, CH_3 10 and CH_3 9), 1.16 (m, 2H, H2), 0.80 (d, $J = 5.8$ Hz, 3H, CH_3 11); ^{13}C-NMR ($CDCl_3$): δ 173.5 (C1), 82.3 (C8), 41.1 (C7), 37.0 (C5), 33.4 and 32.3 (C2, C3 and C4), 26.1 (C10 and C9), 21.3 (C11), 19.3 (C6);); IR (neat): 1729 (C=O); MS, m/z (relative intensity, %): 185 [M^+ 1, 3], 184 (M, 6), 97 (19), 43 (34), 41 (100). Anal. Calc. for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94; O, 17.36. Found: C, 70.89; H, 11.72; O, 16.59%.

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References

[1] (a) G. Consiglio, M. Marchetti, Chimia 30 (1976) 26;
(b) T. Hiyama, N. Wakasa, T. Kusumoto, Synlett (1991) 569;
(c) B. El Ali, H. Alper, J. Mol. Catal. A: Chem. 96 (1995) 197.
[2] (a) J.F. Knifton, J. Org. Chem. 41 (1976) 2885;
(b) G. Cavinato, L. Toniolo, J. Mol. Catal. 10 (1981) 161;
(c) I. Cipres, J. Jenck, Ph. Kalck, J. Mol. Catal. 58 (1990) 387;
(d) L.L. da Rocha, A.O. Dias, E.N. dos Santos, R. Augusti, E.V. Gusevskaya, J. Mol. Catal. A: Chem. 132 (1998) 213;
(e) M.C. Bonnet, A.L. Monteiro, I. Tkatchenko, J. Mol. Catal. A: Chem. 143 (1999) 131;
(f) M.C. Bonnet, N. Carmona, I. Tkatchenko, J. Mol. Catal. A: Chem. 143 (1999) 181.
[3] (a) M. Gomez, G. Muller, D. Sainz, J. Sales, Organometallics 10 (1991) 4036;
(b) E.V. Gusevskaya, E.N. dos Santos, R. Augusti, A.O. Dias, C.M. Foca, J. Mol. Catal. A: Chem. 152 (2000) 15.
[4] J.V. Kingston, G.R. Scollary, J. Chem. Soc. (A) (1971) 3765.
[5] K.H.A. Ostoja Starzewski, P.S. Pregosin, H. Rüegger, Helv. Chim. Acta 65 (1982) 785.
[6] (a) S. Naili, J.F. Carpentier, F. Agbossou, A. Mortreux, G. Nowogrocki, J.P. Wignacourt, New J. Chem. 21 (1997) 919;
(b) L.L. da Rocha, A.O. Dias, E.N. dos Santos, R. Augusti, E.V. Gusevskaya, J. Mol. Catal. A: Chem. 132 (1998) 213.
[7] (a) G. Cavinato, L. Toniolo, Chimia 33 (1979) 286;
(b) R. Bardi, A. del Pra, A.M. Piazzesi, L. Toniolo, Inorg. Chimi. Acta 35 (1979) L345;
(c) R. Bertani, G. Cavinato, L. Toniolo, G. Vasapollo, J. Mol. Catal. 84 (1993) 165.
[8] (a) B. El Ali, H. Alper, J. Mol. Catal. 77 (1992) 7;
(b) K. Kudo, K. Mitsuhashi, S. Mori, K. Komatsu, N. Sugita, Chem. Lett. (1993) 1615;
(c) K. Kudo, Y. Oida, K. Mitsuhashi, S. Mori, K. Komatsu, N. Sugita, Bull. Chem. Soc. Jpn. 69 (1996) 1337.
[9] (a) T. Chenal, I. Cipres, J. Jenck, Ph. Kalck, Y. Peres, J. Mol. Catal. 78 (1993) 351;
(b) T. Chenal, R. Naigre, I. Cipres, Ph. Kalck, J.C. Daran, J. Vaissermann, J. Chem. Soc. Chem. Commun. 9 (1993) 747;

(c) R. Naigre, T. Chenal, I. Cipres, Ph. Kalck, J.C. Daran, J. Vaissermann, J. Organomet. Chem. 480 (1994) 91.
[10] See for instance: S. Akutagawa, in: E.N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), Comprehensive Asymmetric Catalysis, Springer–Verlag, Berlin, 1999, p. 813.
[11] G. Lenoble, R. Naigre, T. Chenal, M. Urrutigoïty, J.C. Daran, Ph. Kalck, Tetrahedron: Asymmetry 10 (1999) 929.
[12] G. Lenoble, M. Urrutigoïty, Ph. Kalck, Tetrahedron Lett. 42 (2001) 3697.
[13] D.R. Coulson, L.C. Satek, S.O. Orim, Inorg. Synth. 13 (1972) 121.