NUCLEOPHILIC SUBSTITUTION REACTIONS OF ALLYLIC ESTERS CATALYSED BY PALLADIUM-GRAPHITE AND RELATED HETEROGENEOUS CATALYSTS

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Summary

Highly dispersed palladium on graphite (Pd/Gr), carbon (Pd/C) and alumina (Pd/Al$_2$O$_3$) have been employed as catalysts in substitution reactions of allylic esters with nucleophiles such as benzenesulfinate and diethyl malonate anions, and 1-(1-cyclohexen-1-yl)pyrrolidine.

Introduction

Among transition metals, palladium holds a useful role in synthetic organic chemistry, since it displays beneficial effects in terms of chemo- and stereo-selectivity in a number of reactions [1]. Homogeneous palladium(0) and palladium(II) species are mostly employed in the synthesis of fine chemicals, since they are more selective and allow the use of milder experimental conditions than heterogeneous catalysts, which consist of palladium supported on inorganic matrices, commonly employed in hydrogenation reactions [2].

Nevertheless, the use of heterogeneous catalysts solves the problem of their separation from the reaction products, and the recovered catalyst can possibly be regenerated and recycled with little loss of activity. Because of these advantages, some efforts have been addressed to find new applications of the common heterogeneous catalysts, especially Pd/C [3], Pd black [4], and Pd amalgam [5], as well as to prepare more active catalysts by anchoring palladium onto inorganic oxides or organic polymers [6]. In particular, palladium anchored onto phosphinated polystyrene resins has found useful applications in carbon–carbon bond-forming reactions [7,8]. Relatively few examples of allylic substitution reactions have been reported which make use of palladium supported on silica, phosphinated polystyrene resin, or carbon [8].

Active palladium has been prepared as a slurry by the reduction of palladium chloride with potassium in the presence of triethylphosphine, or by lithium and

naphthalene [9]. Analogous reductions of the intercalation compound $PdCl_2$–graphite afford palladium–graphite compounds [10].

A few years ago we reported a quite simple method for reducing transition metal halides with potassium–graphite (C_8K) [11]. More recently we have prepared highly dispersed palladium on graphite (Pd–Gr, $C_{16}Pd$) by the same procedure in anhydrous dimethoxyethane (DME) at reflux under argon (eq. 1). Pd–Gr was found active in the catalytic semi-hydrogenation of alkynes [12a] and in vinylic substitution reactions [12b].

$$PdCl_2 + 2\,C_8K \rightarrow C_{16}Pd + 2\,KCl \qquad (1)$$

Preparation of highly dispersed palladium on graphite (Pd–Gr)

A 100 ml flask, equipped with a magnetic stirring bar, reflux condenser, and an argon inlet, previously flamed under an argon flow, was charged with graphite (1.97 g, 164 mmol). This was heated at 130 °C (oil bath) and potassium (0.78 g, 20 mmol) was added in small pieces with stirring. After 15 min the bronze-coloured potassium–graphite was cooled to room temperature and covered with anhydrous tetrahydrofuran (THF, 50 ml), and then $PdCl_2$ (1.77 g, 10 mmol) was added. The slurry was stirred in the refluxing solvent for 8 h, cooled to room temperature, water (2 ml) was added and the solid phase was filtered off using a sintered glass funnel and washed consecutively with 0.1 *M* (HCl (20 ml), hot water (100 ml), methanol (20 ml), and ether (20 ml), and then dried at 0.1 mmHg for 2 h at 80°C. The weight of the black powder obtained (2.84 g) was consistent with an 30.6% palladium loading, excluding any mechanical losses. Different samples prepared by the same procedure, in some cases substituting DME for THF, were analysed by complexometric titration [13], following dissolution of the Pd with concentrated HCl-HNO_3 mixtures (3 : 1). This gave an average palladium content of $31 \pm 2\%$ by weight. The catalyst is air-stable and can be stored for a long time without loss of activity.

Results and discussion

We now report that Pd–Gr activates allylic esters towards nucleophiles in substitution reactions whose simplified mechanism is shown in eq. 2 [1b].

$$\qquad (2)$$

The nucleophiles employed in this study are sodium benzenesulfinate, sodium and potassium diethyl malonate and 1-(1-cyclohexen-1-yl)pyrrolidine. The results obtained using Pd–Gr and the related heterogeneous catalysts Pd/C and Pd/Al_2O_3, as well as $Pd(PPh_3)_4$ and $PdCl_2$ have been compared.

Pd-catalysed reactions of allylic esters with sodium benzenesulfinate

A series of reactions of allylic esters, Ia–Ie, IV, VII and X with sodium benzenesulfinate in the presence of palladium catalysts and triphenylphosphine as ligand were carried out in order to determine: (a) the relative activities of the catalysts, (b) the possibility of recovering and reusing the catalyst, (c) the order of

reactivity of different esters, (d) suitable reaction conditions in the absence of ligand, and (e) the regioselectivity in the attack on unsymmetrically-substituted allylic esters.

The reaction between allyl acetate (Ia) and the sulfinate (eq. 3), in the presence of catalytic amounts of Pd–Gr (2 mol%) and PPh_3 (2 mol%), afforded allyl phenyl sulfone (II) in quantitative yield after stirring in refluxing THF/H_2O for 30 min (Table 1). The possibility of reusing the catalyst is noteworthy. In fact, the reaction was repeated under identical conditions in an apparatus provided with a sintered glass filter and a stopcock in the side arm, which allowed the catalyst to be recovered by filtration and recycled. After ten runs the product yield was 93%, showing that the catalyst loses its activity relatively slowly. The catalyst was successively employed in reactions with different substrates for 28 h in aggregate, and then a repeated preparation of II was accomplished in 47% yield.

Working under argon has only a slight influence on the yield. For example, using 1 mol% of Pd–Gr and 2 mol% of PPh_3, the yields of II obtained in the air and in argon were 86 and 93%, respectively.

Using the same mol ratio we carried out parallel experiments with 10% Pd/C, 10% Pd/Al_2O_3, and $PdCl_2$ (commercial samples), obtaining yields of 68, 85 and 86%, respectively (Table 1). The sulfone obtained from reactions with heterogeneous catalysts was contaminated only by triphenylphosphine, whereas that from the reaction with $PdCl_2$ contained a more polar compound (TLC analysis), which was probably a complex formed between $PdCl_2$, $PhSO_2Na$ and PPh_3 [14], and was purified by column chromatography on silica gel.

In a series of parallel preparations of the sulfone II starting from different allyl

TABLE 1

Pd–Gr-CATALYSED REACTIONS OF ALLYL ESTERS (I) WITH SODIUM BENZENE-SULFINATE IN THE PRESENCE OF TRIPHENYLPHOSPHINE[a]

Ester	Pd (mol%)	PPh_3 (mol%)	Yield of II[b] (%)
Ia	2	2	100
Ia	1	2	86[c] (68)[d] (85)[e] (86)[f]
Ia	0.5	1	35
Ib	0.5	1	65
Ic	0.5	1	78
Id	0.5	1	90
Ie	0.5	1	93[g]

[a] All the reactions were carried out on 10 mmol of ester and 11 mmol of $PhSO_2Na$ in THF/H_2O (18/2 ml) at reflux for 30 min. [b] The yields of II from the reactions with volatile Ia was evaluated from the weight of the crude reaction product by withdrawing the weight of PPh_3 initially added; when starting esters (Ib–Id) were present in the crude reaction products the yields were determined by NMR analysis. [c] The typical experimental procedure is as follows. Allyl acetate (Ia, 1.0 g, 10 mmol), $PhSO_2Na$ (1.8 g, 11 mmol), Pd–Gr (35 mg, 0.1 mmol), and PPh_3 (52 mg, 0.2 mmol) are magnetically stirred in THF/H_2O (18/2 ml) at reflux for 30 min. After cooling to room temperature, the reaction mixture is filtered and the solid phase washed with ether (50 ml). The organic phase is washed with brine and dried (Na_2SO_4), and the solvent is removed under reduced pressure to leave the sulfone II (1.62 g), with PPh_3 the only impurity (TLC); ^1H NMR ($CDCl_3$, TMS): δ 7.5–8.1 (m, 5H, Ph), 4.8–6.1 (m, 3H, CH=CH_2), 2.9 (d, 2H, CH_2) ppm. [d] 10% Pd/C was used as catalyst. [e] 10% Pd/Al_2O_3 was used as catalyst. [f] $PdCl_2$ was used as catalyst. [g] Because of the presence of phenol, the filtered reaction mixture was washed with 10% aqueous NaOH; II contained 10% of isomer III as impurity.

esters, using low relative amounts of Pd–Gr (0.5 mol%) and PPh$_3$ (1 mol%), the yield increased in going from the acetate Ia to the phosphates Ib and Ic, and more again to the carbonates Id and Ie (Table 1). Better leaving groups have a marked effect on the reaction rate, suggesting that the first step in eq. 1 is rate-determining. The successful use of allylic carbonates [15] and phosphates [16] in Pd-catalysed reactions has been reported. As concerns the use of the carbonates Id and Ie, heating them in THF at reflux with Pd–Gr (2 mol%) and PPh$_3$ (4 mol%) caused their conversion to allyl methyl ether and allyl phenyl ether, respectively. This process [15,17] was complete within 30 min for Ie, but was quite slow for Id; however, it was not competitive in the presence of sulfinate.

$$
\text{(I)} \quad \diagdown\diagup\text{OR} \xrightarrow[\text{Pd}-\text{Gr, PPh}_3]{\text{PhSO}_2\text{Na}} \diagdown\diagup\text{SO}_2\text{Ph} \quad \text{(II)} \qquad (3)
$$
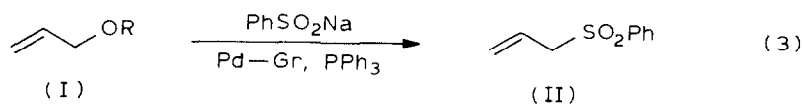
(a . R = COMe ,
  b   R = P(O)(OEt)$_2$;
  c   R = P(O)(OPh)$_2$,
  d   R = CO$_2$Me ,
  e   R = CO$_2$Ph)

We have looked for conditions which allow the preparation of II in the absence of the phosphine, in order to avoid the need for any purification of the reaction product, by working on Ia at higher temperature in suitable solvents. The reactions carried out at 100°C for several hours in dioxane, propionitrile, 1-propanol and 2-butanol gave low yields of II, but the use of water and especially of N,N-dimethyl-formamide (DMF) as solvent afforded more satisfactory results (Table 2). After 8 h in water at 100°C the yield of II was 65%, while a 60% yield was obtained in DMF after only 1 h at the same temperature. The effectiveness of these two solvents can be explained only in part by their ability to solubilize the sulfinate. However in DMF, more markedly at its boiling point, the product II was largely isomerized to (E)-1-propen-1-yl phenyl sulfone (III) (eq. 4).

$$
\text{(II)} \quad \diagdown\diagup\text{SO}_2\text{Ph} \; \underset{\longleftarrow}{\overset{\text{base}}{\longrightarrow}} \; \diagdown\diagup\text{SO}_2\text{Ph} \quad \text{(III)} \qquad (4)
$$
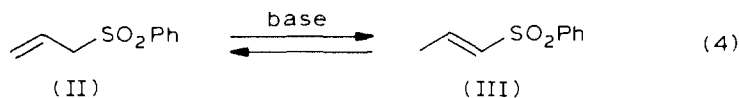
The same isomerisation occurred to a certain extent in the reactions performed in THF/H$_2$O/PPh$_3$ on Ie (Table 1) and on Ia if the amount of H$_2$O was greatly reduced. The degree of isomerisation is dependent on the basicity of the anion liberated in the formation of the (π-allyl)palladium complex, i.e. acetate from Ia and phenoxide from Ie, and increases with temperature and the reaction time [18,19].

While DMF is essential to a satisfactory reaction rate, the presence of water reduces the isomerisation of II, but also the reaction rate. A compromise can be obtained by using them in a 1:1 ratio, since II was isolated in 75% yield, contaminated by 3% of III, after the reaction had been heated for 1 h at 100°C. Even in these experimental conditions Pd/C has a comparable, but slightly lower activity relative to Pd–Gr. PdCl$_2$, although giving the same yield, caused more isomerisation of II to III [20].

TABLE 2

Pd–Gr CATALYSED REACTIONS OF ALLYL ACETATE (Ia) WITH SODIUM BENZENE-SULFINATE IN THE ABSENCE OF TRIPHENYLPHOSPHINE[a]

Solvent (ml)	Conditions		Yield[b] (%)	II/III[c]
	T (°C)	t (h)		
H_2O (10)	100	8	65	100/0
DMF (10)	100	1	60	60/40
DMF (10)	155	1	88	28/72
H_2O/DMF (9/1)	100	6	90 (76)[d]	99/1
H_2O/DMF (5/5)	100	1	75[e]	97/3
DMF/H_2O (8/2)	100	1	87 (87)[f]	85/15 (60/40)[f]

[a] All reactions were carried out on 10 mmol of Ia and 11 mmol of $PhSO_2Na$ in 10 ml of solvent, using 2 mol% of catalyst. [b] Isolated yield. [c] Isomer ratio determined by ^1H NMR analysis of the reaction product, integrating the peak areas of the allylic protons of the two isomers. The δ-values ($CDCl_3$, TMS) of III are: 7.5–8.0 (m, 5H, Ph), 6.85 (m, CH_3–CH=, 1H), 6.45 (m, 1H, SO_2CH=), 1.85 (d, 3H, CH_3) ppm. [d] 10% Pd/C was used as catalyst. [e] The typical experimental procedure is as follows. Allyl acetate (Ia, 1.0 g, 10 mmol), $PhSO_2Na$ (1.8 g, 11 mmol) and Pd–Gr (70 mg, 0.2 mmol) are magnetically stirred in DMF/H_2O (5/5 ml) at 100 °C (water bath) for 1 h. After cooling to room temperature, the reaction mixture is filtered and the solid phase washed with water (10 ml), 10% aqueous HCl (3 × 10 ml) to remove DMF, then with brine, and dried (Na_2SO_4). The solvent is removed under reduced pressure to give the sulfone II (1.36 g, 75%, 97% pure). [f] $PdCl_2$ was used as catalyst: a black precipitate was formed after 30 min.

A few checks have been carried out to determine the degree of regioselectivity of Pd-Gr-catalysed reactions of sodium benzenesulfinate with unsymmetrically-sub-stituted allylic esters in usual conditions (10 mmol scale, refluxing THF/H_2O (18/2 ml), 2 mol% of Pd–Gr, 4 mol% of PPh_3), by monitoring the reactions by GLC analysis.

1-Octen-3-yl acetate (IV) was converted after 20 h to a mixture of E,Z-2-octen-1-yl phenyl sulfone (V) and 1-octen-3-yl phenyl sulfone (VI) (eq. 5) in 96% isolated yield with an isomer ratio E-V/Z-V/VI of 80 : 11 : 9, as evaluated by GLC analysis performed on a SE52 glass capillary column (20 m, film thickness 0.1 – 0.15 μ, retention times at 180°C: 7.45, 7.27 and 5.59 min, respectively). The ^1H NMR spectrum of the reaction product showed the absorptions of the two·regioisomers, in particular at ($CDCl_3$, TMS): δ 3.8 (m, CH_2SO_2) and 5.5 (m, CH=CH) for V, and at 3.5 (m, $CHSO_2$) and 4.8 – 5.8 (m, CH=CH) ppm for VI [21].
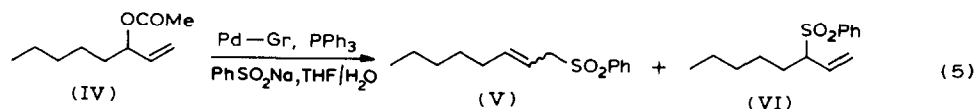

A complete regiospecificity was accomplished using the homogeneous catalyst $Pd(PPh_3)_4$ under argon at room temperature overnight, or in refluxing THF/H_2O (18/2) after 1 h: the sulfone V was infact isolated in 97 and 94% yield, respectively, with an E/Z ratio of 89/11. It was previously reported [22] that the product from the attack of the sulfinate anion at the more substituted site of (π-allyl)palladium complexes is kinetically favoured, but is then converted to the thermodynamically more stable product, through a similar (π-allyl)palladium complex. For Pd–Gr, the conversion of the acetate IV to the sulfones V and VI was quantitatively accom-

plished after 2 h (V/VI = 55/45), but the isomerisation of VI to V was much slower than in the case of $Pd(PPh_3)_4$ [23].

Similarly, starting from geranyl acetate (VII, mixed isomers) a mixture of geranyl, neryl and linalyl sulfones (E-VIII, Z-VIII and IX, respectively) was obtained (eq. 6), using Pd–Gr (2 mol%) – PPh_3 (5 mol%) as catalyst. The sulfone IX, initially predominating, was almost completely converted after 30 h to E,Z-VIII. The product, isolated in 89% yield, had the following composition by GLC analysis at 190°C on an SE52 glass capillary column (20 m, film thickness 0.1 – 0.15 μ, retention times in parenthesis): E-VIII, 74% (9.75); Z-VIII, 20% (8.78); IX, 2.5% (7.69); other impurities, 3.5%; ^1H NMR ($CDCl_3$, TMS): δ 7.5–8.1 (m, 5H, Ph), 5.1 (m, 2H, CH=), 3.8 (d, 2H, CH_2SO_2), 2.0 (m, 4H, CH_2CH_2), 1.7, 1.6 and 1.3 (s, 3H, CH_3) ppm.
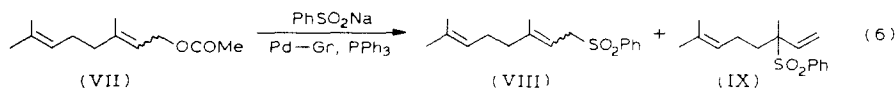
The reaction of sorbyl acetate (X), catalysed by a sample of Pd–Gr recovered from previous runs on Ia, afforded after 3 h a mixture of the isomeric sulfones XI, XII and XIII (eq. 7) in 98% overall yield, having an isomer composition (GLC analysis on an SE52 glass capillary column at 170 °C, retention times in parenthesis): XI 60% (6.39); XII 10% (6.18); XIII 30% (4.57). The relative ratio was only slightly affected by prolonged heating, even with a fresh catalyst. Crystallisation from ether afforded a sample of XI containing 4% of XIII, by GLC analysis: m.p. 83°C: ^1H NMR ($CDCl_3$, TMS): δ 7.5 – 8.1 (m, 5H, Ph), 5.3 – 6.4 (m, 4H, CH=), 3.8 (d, 2H, CH_2SO_2), 1.7 (s, 3H, CH_3) ppm. The spectrum of the crude reaction product also showed absorptions at 4.8–6.0 (m, CH=), 3.9 (m, $CHSO_2$), and 1.45 (d, CH_3) ppm, which have been attributed to the regioisomer XIII because of the similarity to those of known α-substituted allyl phenyl sulfones [24]. The formation of the α- and γ-regioisomers in Pd-catalysed nucleophilic attack on sorbyl acetate has been reported [8b].
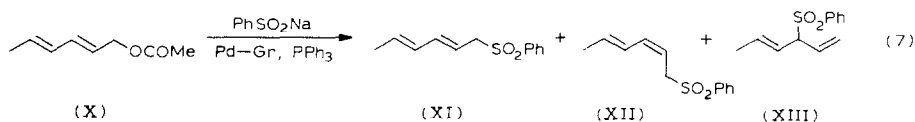
Pd-catalysed reactions of allylic esters with carbon nucleophiles

The Pd-catalysed formation of carbon–carbon bonds has gained a particular importance in synthetic organic chemistry. This goal is usually achieved by activating allylic acetates towards soft nucleophiles such as the carbanions derived from malonic, acetoacetic and α-sulfonyl esters, and so on [25]. Furthermore, starting from allylic carbonates [15] and 1,3-diene mono-epoxides [19,26], such reactions can be performed under neutral conditions.

The carbanion formed from diethyl malonate (XIV) can be allylated with allyl esters (I) (eq. 8), using catalytic amounts of Pd–Gr and PPh_3 (Table 3).
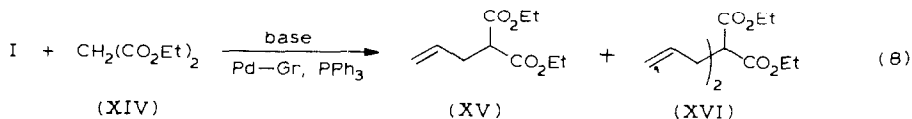
When the carbanion was prepared previously, by treatment of XIV with one equivalent of sodium hydride in anhydrous THF, the reaction with allyl acetate (Ia) occurred with good conversion but produced both the monoallyl and diallyl derivatives XV and XVI, respectively. Forming the carbanion "in situ" by means of excess potassium carbonate drastically reduced the yield of the diallylated compound, even more so when the malonate was also used in excess. The reaction could also be performed in refluxing toluene in a shorter reaction time: the presence of a small amount of triethylbenzylammonium chloride (TEBA) had only a slight influence. The greater reactivity of diethyl allyl phosphate (Ib) compared to the acetate Ia, already observed in the reaction with $PhSO_2Na$, was confirmed, since under the same conditions diethyl allyl malonate (XV) was obtained from Ib in slightly higher yield and in a shorter reaction time.

On the other hand, the use of the carbonates Id and Ie in the absence of the base gave less satisfactory results, probably because the formation of an allyl ether (allyl phenyl ether was observed in the reaction mixture obtained from Ie) was a process competitive with sequential metallation of XIV and the C–C bond-forming reaction.

Enamines, synthetic equivalents of enolates, are known to react under palladium catalysis with allylic derivatives, giving rise to α-allylated and α,α'-allylated carbonyl compounds [27].

The allylic esters Ia, Ib (5 mmol) reacted with 1.5 equivalents of 1-(1-cyclohexen-1-yl)pyrrolidine (XVII) in anhydrous THF under reflux in the presence of catalytic amounts of Pd–Gr (2 mol%) and PPh_3 (8 mol%) to give good yields of 2-allylcyclo-
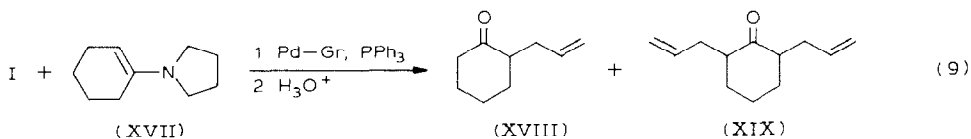
TABLE 3

Pd–Gr CATALYSED ALLYLATION OF DIETHYL MALONATE (XIV) [a]

Ester	Base	Mol ratio (I/XIV/base)	Reaction time (h)	Yield (%) [b]	
				XV	XVI
Ia	NaH [c]	1/1/1	6	42	27
Ia	K_2CO_3	1/1/3	6	47	3
Ia	K_2CO_3	1/2/6	8	61 [d]	3
Ia	K_2CO_3	1/1.5/2.5	2	55 [e] (48) [f]	3 [e] (2) [f]
Ib	K_2CO_3	1/1/3	2	52	7
Id	–	1/1	4	41	3
Ie	–	1/1	8	27 [g]	1

[a] Unless otherwise stated, the reactions were performed on 5 mmol of ester 1 in anhydrous THF at reflux under argon, using 2 mol% of Pd–Gr and 8 mol% of PPh_3. [b] The yields were evaluated by GLC analyses on a OV1 glass capillary column (20 m, film thickness 0.1–0.15 μ) using n-dodecane as internal standard; the retention times at 85°C were: 1.55 (XIV), 3.84 (XV), 10.46 (XVI) min. The yield of the diallylated compound is based on I. The products were identified by comparison with authentic specimens. [c] Sodium diethyl malonate was preformed by the addition of NaH (1 equiv.) to XIV. [d] The typical experimental procedure is as follows. Allyl acetate (Ia, 0.5 g, 5 mmol), diethyl malonate (XIV, 1.62 g, 10 mmol), anhydrous K_2CO_3 (4.15 g, 30 mmol, previously dried at 80°C under reduced pressure for 5 h), Pd–Gr (35 mg, 0.1 mmol), PPh_3 (102 mg, 0.4 mmol) and n-dodecane (0.375 g) are magnetically stirred in anhydrous THF (10 ml) at reflux under argon for 8 h. The reaction mixture is cooled, diluted with ether (50 ml), quenched with 30% aqueous HCl (5 ml) and filtered. The organic phase is separated, dried and analysed. [e] The reaction was performed in toluene at 100°C (oil bath) under argon in the presence of TEBA (148 mg, 0.65 mmol). [f] Allyl phenyl ether was identified in the reaction mixture by GLC comparison with an authentic specimen.

hexanone (XVIII), accompanied by small amounts of 2,6-diallylcyclohexanone (XIX) (eq. 9, Table 4). Even in this reaction Ib was more reactive than Ia. Pd/C can also

$$I \ + \ \underset{(XVII)}{\text{cyclohexenyl-pyrrolidine}} \quad \xrightarrow[2\ H_3O^+]{1\ Pd-Gr,\ PPh_3} \quad \underset{(XVIII)}{\text{allylcyclohexanone}} \ + \ \underset{(XIX)}{\text{diallylcyclohexanone}} \qquad (9)$$

be conveniently employed. In fact, under the usual experimental conditions (2 mmol% of Pd, 8 mol% of PPh_3, THF at reflux under argon, 5 mmol scale) the reaction of 1-octen-3-yl acetate (IV) with the enamine XVII (1.5 equiv.) afforded after 3 h, following acidic quenching and column chromatography on silica gel, 2-(2-octen-1-yl)cyclohexanone (XX) in 72% yield (eq. 10). GLC analysis on a glass

$$IV \ + \ XVII \quad \xrightarrow[2\ H_3O^+]{1\ Pd-Gr,\ PPh_3} \quad \underset{(XX)}{\text{2-(2-octen-1-yl)cyclohexanone}} \qquad (10)$$
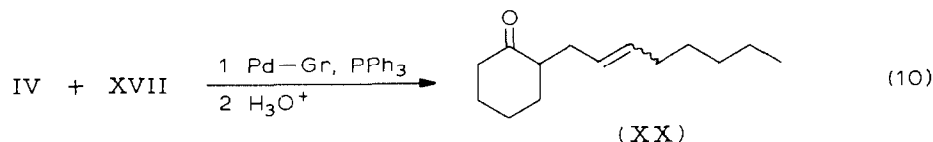
capillary Carbowax column (25 m) at 140°C showed that the product was a mixture of E and Z isomers in a 91/9 ratio; ^{1}H NMR (CDCl$_3$, TMS): δ 5.35 (m, 2H, CH=), 1.5–2.6 (m, 13H, ring and allylic H), 1.25 (m, 6H, aliphatic), 0.9 (t, 3H, CH$_3$) ppm; MS, m/e 208 (M^+), 98.

Experimental

Materials

Potassium (99.5%), anhydrous potassium carbonate and diethyl malonate (XIV) were from Carlo Erba. Graphite was obtained from Roth. Palladium chloride.

TABLE 4

Pd–Gr CATALYSED ALLYLATION OF 1-(1-CYCLOHEXEN-1-YL)PYRROLIDINE (XVII)[a]

Ester	Mol ratio of reagents (I/XVII)	Time (h)	Yield[b] (%)	
			XVIII	XIX
Ia	1/1.5	8	81	7
Ib	1/1.5	2	82[c]	7
Ib	1/1.1	2	73	16

[a] All the reaction have been performed on 5 mmol of ester I in anhydrous THF under argon, using 2 mol% of Pd–Gr and 8 mol% of PPh$_3$. [b] The yields were evaluated by GLC analysis using n-dodecane as internal standard on a 0V1 glass capillary column (20 m, film thickness 0.1–0.15 μ), the retention times at 90°C were: 1.78 (XVIII), 5.54 (XIX). The yield of XIX is based on I. [c] The typical experimental procedure is as follows. Diethyl allyl phosphate (Ib, 0.98 g, 5 mmol), 1-(1-cyclohexen-1-yl)pyrrolidine (XVII, 1.13 g, 7.5 mmol), Pd–Gr (35 mg, 0.1 mmol), PPh$_3$ (102 mg, 0.4 mmol), and n-dodecane (0 375 g) are magnetically stirred in anhydrous THF (20 ml) at reflux for 2 h under argon The reaction mixture is cooled, quenched with 10% aqeuous HCl, and filtered. The organic phase is extracted with ether, dried (Na$_2$SO$_4$) and analysed by GLC, which indicates an 82% yield of XVIII and 7% yield of XIX. A pure sample of XVIII is obtained by column chromatography on silica gel: IR: 1710, 1640 cm^{-1}; ^{1}H NMR (CDCl$_3$, TMS): δ 4.8–6.2 (m, 3H, CH=CH$_2$), 1.5–2.6 (m, 11H, ring and allylic H) ppm

tetrakis(triphenylphosphine)palladium, 10% Pd/C, 10% Pd/Al$_2$O$_3$, triphenylphosphine, sodium benzenesulfinate, allyl acetate (Ia), geranyl acetate (VII), and 1-(1-cyclohexen-1-yl)pyrrolidine (XVII) were purchased from Fluka, as were allyl alcohol, 1-octen-3-ol, methyl chloroformate, phenyl chloroformate, diethyl chlorophosphate, diphenyl chlorophosphate, which were the starting materials for the preparation of the esters Ib–Ie and IV, by standard procedures. Sorbyl acetate (X) was from ICN.

Solvents

Anhydrous tetrahydrofuran (THF) was distilled over sodium benzophenone ketyl under argon. Toluene was distilled over sodium under argon. *N,N*-Dimethylformamide (DMF) was distilled over molecular sieves.

Analysis

^{1}H NMR spectra were recorded at 60 MHz on a Perkin–Elmer R12B spectrometer. Mass spectra (MS) were recorded on a Varian MAT 111 instrument at 70 eV. Gas chromatographic analyses were carried out on a Carlo Erba Fractovap apparatus. Column chromatography was performed on silica gel (Merck, 230–400 ASTM) using hexane/ether or hexane/ethyl acetate mixtures as the eluent. Melting points (m.p.) are uncorrected.

Acknowledgement

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