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Heck arylation of acrolein acetals using the 9-bromoanthracene: A case of study

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Dedicated to Professor Wolfgang A. Herrmann on the occasion of his 60th birthday.

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ABSTRACT

The influence of several parameters on the selectivity of the palladium catalysed Heck coupling of 9-bromoanthracene with acrolein acetals was studied. While the ester is the quasi exclusive product when only a base (i.e. NaOAc, K_2CO_3, etc.) is added in the medium, the presence of halide abstracting agent such as thallium or silver salts decreases noticeably the selectivity towards the ester. On the other hand, the addition of *n*-Bu_4NOAc yields to the formation of the aldehyde with up to 74% selectivity. The presence of water was found to play a significant role not only on the rate but also on the selectivity of the reaction. A comprehensive mechanism is proposed outlining the influence of each additive, particularly on the selectivity of the reaction.

1. Introduction

Cinnamaldehyde derivatives and 3-arylpropionic acids/esters are important intermediates for the synthesis of elaborated molecules, like antifugal or antibacterial pharmaceuticals and TFN-α inhibitors or lactam antibodies, respectively [1–5]. Together with several groups, we reported the selective Heck arylation of acrolein derivatives to yield either 3-arylpropionic esters or the corresponding cinnamaldehyde derivatives [6–12]. It was found that coupling of aryl halides with acrolein acetals, led either to the formation of cinnamaldehyde derivatives or of 3-arylpropionic esters depending on the reaction conditions. For example, starting from acrolein diethylacetal, Cacchi et al. reported the selective preparation of cinnamaldehyde derivatives in the presence of $Pd(OAc)_2$, K_2CO_3, KCl, *n*-Bu_4NOAc in DMF for a large variety of aryl halides; alternatively, changing the reaction conditions to $Pd(OAc)_2$, *n*-Bu_4NCl, *n*-Bu_3N in DMF, they achieved the selective preparation of esters derivatives [6,7]. Najera et al. described similar studies using the well defined dimeric 4-hydroxyacetophenone oxime-derived palladacycle as the catalyst [8]. In parallel, the selective synthesis of 3-arylpropionic acids was described by the group of Santelli and Doucet starting from acrolein ethylene acetal using the tetradentate TEDICYP (1,2,3,4-tetrakis(diphenylphosphinomethyl)cyclopentane) ligand under somewhat "classical" Heck reaction conditions (TEDICYP ligand, $[Pd(C_3H_5)Cl]_2$ (0.001–0.4 mol%), K_2CO_3, DMF, 110 °C, 20 h). The most impressive outcome concerns the "catalyst/substrate" ratio: at a catalyst/substrate loading as low as 1/10000, the coupling of aryl iodides and some activated aryl bromides with acrolein ethylene acetal gave almost quantitative yields towards the esters after 20 h [11].

We studied these reactions not only in the presence of homogeneous catalysts but also under heterogeneous conditions using the $[Pd(NH_3)_4]$-NaY zeolite as the catalyst [9,10]. Various polyaryl and heteroaryl bromides were involved in these studies; in every cases, when performing the reaction in presence of *n*-Bu_4NOAc cinnamaldehydes were obtained as the main compounds (selectivity ⩾ 85%) except for the coupling of the 9-bromoanthracene that gave a mixture of aldehyde and ester (respectively, 60/40). On the other hand, in the absence of *n*-Bu_4NOAc, 3-arylpropionic esters were selectively produced (>75% selectivity) [6,7,10].

Unexpectedly surprised by the lack of selectivity towards the corresponding cinnamaldehyde when coupling the 9-bromoanthracene with acrolein acetals under optimised conditions (Pd-catalyst, K_2CO_3, *n*-Bu_4NOAc, KCl, DMF, 110 °C), we carried out a detailed study of this specific Heck coupling reaction investigating several reaction parameters. In this contribution, we report the results issued from this study: the optimisation of the reaction conditions to obtain high selectively towards either the 3-anthracyl propionic ester or alternatively the 3-anthracyl acrolein.

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2. Results and discussion

Initially, the Heck arylation of acrolein acetals using the 9-bromoanthracene as the aryl halide (Scheme 1) was carried out under the reaction conditions optimised by Cacchi and co-workers (1.5 equiv. of K_2CO_3, 2 equiv. of *n*-Bu_4NOAc, 1 equiv. of KCl) [7], except that we used a lower olefin excess (1.5 equiv. vs. 3 equiv. for Cacchi) and worked at 110 °C instead of 90 °C.

In the first stage of this study we attached a particular importance to the role played by additives, i.e. ammonium salts and chloride sources, for the Heck coupling reaction of acrolein diethyl acetal ($R_1 = R_2 = Et$) with the 9-bromoanthracene. The influence of the nature of the base complemented this initial step (Table 1, entries 1–10).

Under initial conditions (1 equiv. of 9-bromoanthracene, 1.5 equiv. of acrolein diethylacetal, 1.5 equiv. of K_2CO_3, 2 equiv. of *n*-Bu_4NOAc, 1 equiv. of KCl), complete conversion was achieved with 60% aldehyde selectivity after 1 h (Table 1, entry 1). Only traces of anthracene due to dehalogenation were observed [13]. In the absence of KCl, the selectivity in aldehyde was slightly improved (76%) but at the expense of the reaction rate (Table 1, entry 2). When *n*-Bu_4NOAc was used as the only source of base, the rate of the reaction remains the same as in presence of co-bases (i.e. K_2CO_3) but the selectivity of the reaction towards the aldehyde decreased significantly (44%; entry 3 vs. 76%; entry 2).

Replacing *n*-Bu_4NOAc (entry 3) or K_2CO_3/*n*-Bu_4NOAc (entries 1 and 2) by K_2CO_3 alone (entry 4) resulted in rate acceleration of the reaction as it was completed within 10 min (Table 1 and Fig. 1) instead of 1–5 h in the other cases. Under these conditions the ester was almost the exclusive product (92% selectivity). Identically, the use of the *n*-Bu_4NCl as the ammonium source led to the formation of the ester as the main product (entries 5 and 6).

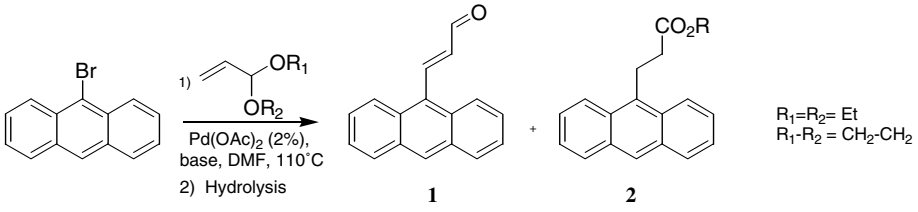
Various bases (NEt_3, NaOAc, $Ca(OH)_2$) were evaluated for this coupling reaction. While no influence was observed in terms on selectivity the aldehyde being in all cases the main product, we observed in all cases lower reactions rates (entries 7–10).

Alternatively, we carried out the coupling reaction of the acrolein ethylene acetal with the 9-bromoanthracene following the report by Doucet and Santelli [11]. In our hands, this substrate exhibited similar selectivities than acrolein diethyl acetal under identical reaction conditions (comparing entry 4 vs. 11; entry 2 vs. 12 and 1 vs. 13).

Kinetic experiments were carried out for the coupling reaction of 9-bromoanthracene with acrolein diethyl acetal in presence and in absence of *n*-Bu_4NOAc, all other reaction conditions being identical (olefin/aryl halide = 1.5, 2 mol% $Pd(OAc)_2$, 1.5 equiv. K_2CO_3, DMF, 110 °C). Fig. 1 clearly shows that the presence of ammonium salts such as *n*-Bu_4NOAc strongly decreases the reaction rate since it required up to 5 h to achieve complete conversion of the 9-bromoanthracene while only 10 min were necessary in absence of this additive. Interestingly, it was observed that a period of induction (15 min) was necessary before the pre-catalyst became active in presence of ammonium source. In both cases, while being opposite (i.e., towards the ester; 92% and 24% in absence and presence of *n*-Bu_4NOAc, respectively) the selectivities of the reactions remained constant all over the reaction time.

In order to optimise further the reaction conditions, the influence of the nature of the solvent was studied (Table 2). Whatever the solvent used, the 9-bromoanthracene was quantitatively transformed at 110 °C using the $Pd(OAc)_2$ as the catalyst, K_2CO_3 as the base, in presence of *n*-Bu_4NOAc. However, it was found that the nature of the solvent played an important role on the ester/aldehyde selectivity. While in the NMP both products were formed in equimolar ratio (entry 1), in DMAc or DMF the aldehyde was mainly obtained (59% and 78%, respectively, entries 2 and 3).

Interestingly, addition of water to the mixture increased the reaction rate in a significant way: without H_2O complete conversion was achieved after 5 h (entry 3) while by adding 0.1–1 ml of



Scheme 1. Heck coupling of the 9-bromoanthracene with acrolein acetals.

Table 1
Influence of bases and additives on the selectivity of the Heck arylation of the acrolein acetals with 9-bromoanthracene[a]

Entry	Reaction conditions	Time (h)	Conv.(%)	**2**/**1** selectivity
1[c]	K_2CO_3 (1.5 equiv.) *n*-Bu_4NOAc (2 equiv.) KCl (1 equiv.)	1	100	40/**60**
2[c]	K_2CO_3 (1.5 equiv.), *n*-Bu_4NOAc (2 equiv.)	5	100	24/**76**
3	*n*-Bu_4NOAc (2 equiv.)	1	100	**56**/44
4	K_2CO_3 (1.5 equiv.)	0.15	100	**92**/8
5	K_2CO_3 (1.5 equiv.) *n*-Bu_4NCl (1 equiv.)	1.5	100	**98**/2
6	K_2CO_3 (1.5 equiv.) NaOAc (2 equiv.) *n*-Bu_4NCl (1 equiv.)	4.5	98	**90**/10
7	NEt_3 (2 equiv.), K_2CO_3 (1.5 equiv.)	3	98	**98**/2
8[c]	NEt_3 (2 equiv.)	6	25	**90**/10
9	NaOAc (2 equiv.)	4	94	**92**/8
10	$Ca(OH)_2$ (2 equiv.)	6	75	**98**/2
11[b]	K_2CO_3 (1.5 equiv.)	29	73	**98**/2
12[b]	K_2CO_3 (1.5 equiv.), *n*-Bu_4NOAc (2 equiv.)	3	100	26/**74**
13[b]	K_2CO_3 (1.5 equiv.) *n*-Bu_4NOAc (2 equiv.) KCl (1 equiv.)	1	100	42/**58**

The main product selectivity is in bold.
[a] Standard conditions: 9-BrAnt (1 equiv.), acrolein diethyl acetal (1.5 equiv.), $Pd(OAc)_2$ (2%), DMF, 110 °C.
[b] Acrolein ethylene acetal (R_1–$R_2 = CH_2$–CH_2) as substrate.
[c] In these cases dehalogenation (8–15%) was observed.

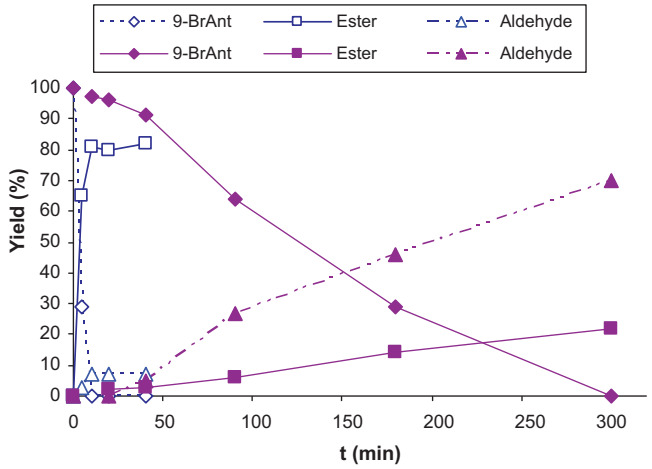


Fig. 1. Evolution of the respective concentration of compounds vs. the time (♦ 9-BrAnt, ▲ aldehyde, ■ ester; without *n*-Bu_4NOAc empty symbols, with *n*-Bu_4NOAc (2 equiv.) plain symbols). Reaction conditions: 9-BrAnt (1 equiv.), acrolein diethyl acetal (1.5 equiv.), $Pd(OAc)_2$ (2%), DMF, 110 °C.

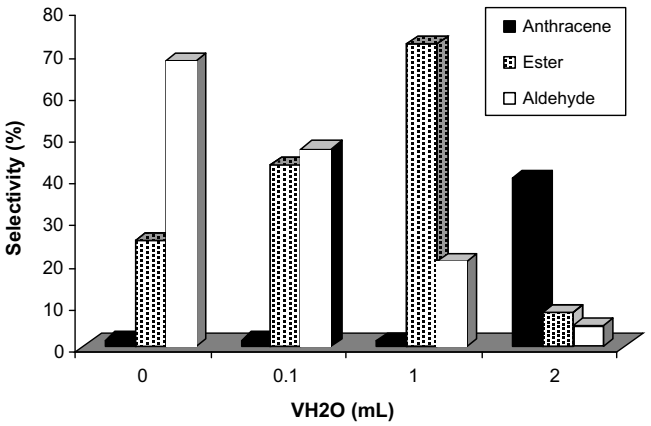


Fig. 2. Influence of water added amounts on the selectivity of the arylation of the acrolein diethyl acetal with 9-bromoanthracene. Reaction conditions: 9-BrAnt (1 equiv.), acrolein diethyl acetal (1.5 equiv.), $Pd(OAc)_2$ (2%), K_2CO_3 (1.5 equiv.), *n*-Bu_4NOAc (2 equiv.), DMF (3 mL), 110 °C.

Table 2
Influence of the nature of the solvent on the selectivity of the Heck arylation of the acrolein diethyl acetal with the 9-bromoanthracene[a]

Entry	Solvent	*t* (min)	Conversion (%)	**2**/**1** selectivity
1	NMP	150	100	53/47
2	DMAc	150	100	41/59
3	DMF	300	100	24/78
4	DMF/H_2O (30/1)	20	100	48/52
5	DMF/H_2O (3/1)	15	99	84/16
6	DMF/H_2O (3/2)	1440	100	[b]
7	Toluene/H_2O (1/1)	150	100	99/1

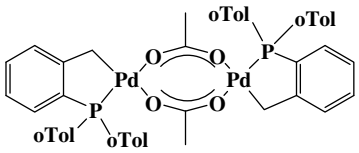
[a] Standard conditions: 9-BrAnt (1 equiv.), acrolein diethyl acetal (1.5 equiv.), $Pd(OAc)_2$ (2%), K_2CO_3 (1.5 equiv.), *n*-Bu_4NOAc (2 equiv.), solvent (3 mL), 110 °C.
[b] Not significant due to the large amount of dehalogenation product.

water the reaction was ended within 20 min (entries 4 and 5). On the other hand adding larger amount of water led to low reaction rate due to lack of solubility of the reagents in the solvent mixture (entry 6) [14]. Such effect were previously reported for Heck coupling reactions under ligand free conditions [15,16]. As far as the selectivity was concerned, the addition of water to DMF improved noticeably the selectivity towards the ester. As by-product, negligible amount of undesired anthracene due to dehalogenation was observed so long the reaction stayed homogeneous; otherwise dehalogenation became the main reaction and anthracene was formed up to 40% yield (Fig. 2).

Surprisingly, in biphasic conditions complete conversion was achieved within 150 min (entry 7), a result that can be reasonably attributed to the presence of *n*-Bu_4NOAc which can act as phase transfer agent.

Whereas the previous optimisations gave up reaction conditions to prepare selectively and in good yields the 3-anthracylpropionic ester, none allowed the selective formation of the corresponding unsaturated aldehyde. Since previous studies showed that the direct coupling of 9-bromoanthracene with acrolein was not efficient due to the formation of several by-products [17], it is still needed to find out reactions conditions for the selective preparation of the 3-anthracylacrolein by the Heck reaction.

Therefore, further attempts were related to early reports by Jeffery. She showed that the presence of silver salt affected dramatically the selectivity of the Heck coupling of aryl iodide with allylic alcohol [18]. While the $Pd(OAc)_2/NaHCO_3$/*n*-Bu_4NCl system yielded selectively β-aryl carbonyl compounds, the $Pd(OAc)_2/PPh_3$/AgOAc system afforded mainly the β-aryl-α,β-unsaturated alcohols. This was attributed to the halide dissociating properties of Ag^+.



"Herrmann's Palladacyle"

Fig. 3.

The influence of silver and thallium salts on the selectivity of the coupling reaction of the 9-bromoanthracene with the acrolein diethyl acetal was studied using either the $Pd(OAc)_2$ or the Herrmann's palladacycle (Fig. 3) as catalysts. Results are reported in Table 3.

Compared to studies described above, the preliminary tests performed at 110 °C showed that addition of silver salts lowered the reaction rates (Table 3, entry 2). This effect could be, however, counterbalanced by working at 140 °C.

Addition of $AgBF_4$ strongly decreased the reaction rate: after 6 h only 35% of 9-bromoanthracene was converted vs. 84% after 30 min in absence of $AgBF_4$ (entries 1 and 2). Moreover, the selectivity of the reaction was substantially modified: in absence of salt the ester was predominantly formed while in the presence of silver salt an equimolar mixture of the ester and the aldehyde was obtained. As expected from Jeffery's works, the addition of dissociating agents (i.e. silver salts here) increased the selectivity towards the cinnamaldehyde but not as expected.

Using the Herrmann's palladacycle [19,20] as the catalyst led to similar observations; the addition of silver salts increased the selectivity towards the unsaturated aldehyde (i.e. 35% with vs. 28% without $AgBF_4$; entries 3 and 4) and the reaction rate was lowered. Changing $AgBF_4$ to $AgPF_6$ or Tl_2CO_3 did not affect the selectivity in aldehyde (entries 7 and 8). Only the presence of *n*-Bu_4NOAc allowed the formation of aldehyde as the main product (>65% selectivity, entries 5 and 6).

3. Summary and postulated mechanisms

To outline the influence that each parameter can play on the selectivity of the reaction, we propose the following general

Table 3
Influence of presence of dissociating salts on the selectivity of the Heck arylation of the acrolein diethyl acetal with the 9-bromoanthracene[a]

Entry	Conditions[b]	*t* (h)	Conv. (%)	GC yield (%)			**2**/**1** selectivity
				ArH	**2**	**1**	
1	$Pd(OAc)_2$(2%)	0.5	84	1	82	2	**98**/2
2	$Pd(OAc)_2$(2%) $AgBF_4$ (1 equiv.)	6	35	1	13	13	50/50
		6 (110 °C)	25	3	9	10	50/50
3	Pdcycle (2%)	1	100	2	74	17	**82**/18
4	Pdcycle (2%) $AgBF_4$ (1 equiv.)	1	70	5	40	22	**65**/35
		2.5	100	7	54	23	**70**/30
5	Pdcycle (2%) *n*-Bu_4NOAc (2 equiv.)	1	100	2	28	58	32/**68**
6	Pdcycle (2%) *n*-Bu_4NOAc (2 equiv.) $AgBF_4$ (1 equiv.)	1	100	9	35	49	35/**65**
7	Pdcycle (2%) Tl_2CO_3(1 equiv.)	1	100	2	76	14	**83**/17
8	Pdcycle (2%) $AgPF_6$ (1 equiv.)	1	100	15	62	19	**77**/23

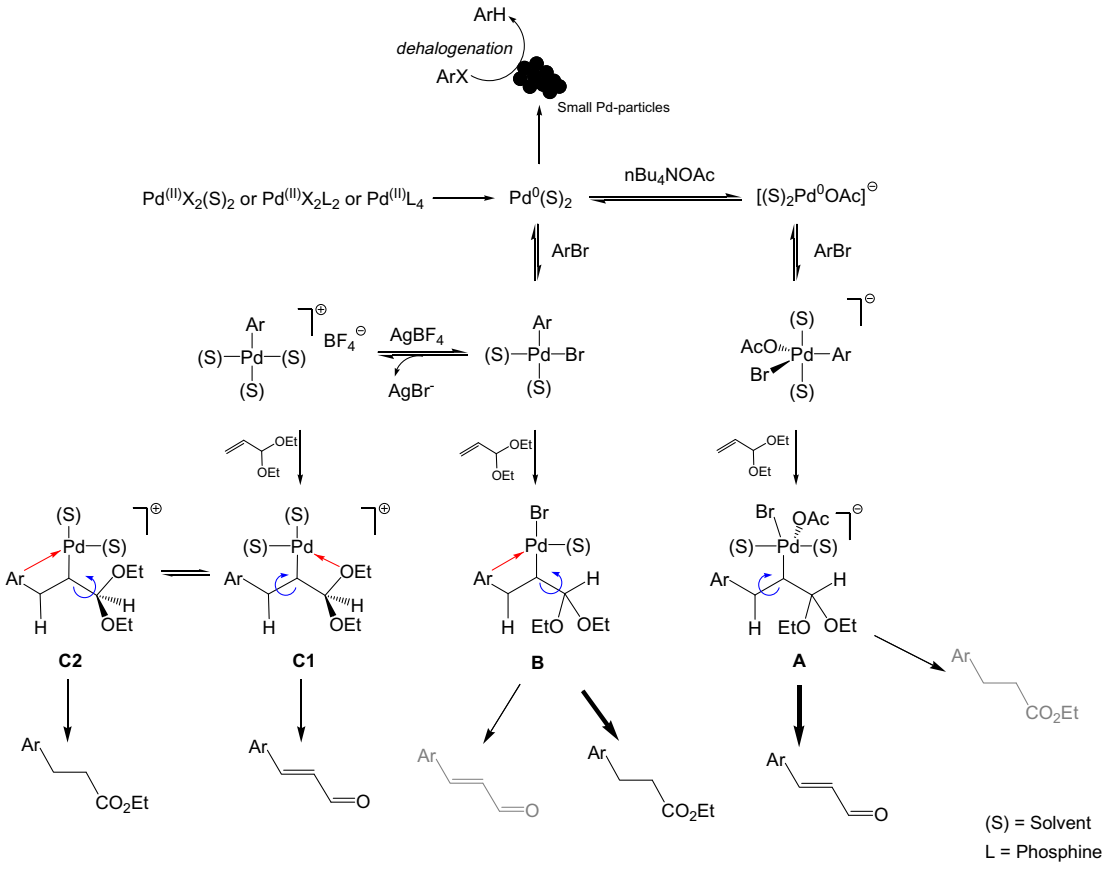
The main product selectivity is in bold.
[a] Standard conditions: K_2CO_3 (1.5 equiv.), DMF, 140 °C.
[b] Pdcycle refer to the Herrmann's palladacycle, Fig. 3.

scheme summarizing these aspects. According to various reports, depending on the additives different intermediate palladium complexes could be involved in the Heck coupling reaction, all of them being depicted in Scheme 2.

As previously suggested, addition of *n*-Bu_4NOAc in the reaction medium favours the formation of anionic catalytic palladium-species **A** that yields β-aryl acroleins [10,21–23]. However, the 9-bromoanthracene represented a specific case for which the rotation around the ArCH–CHPd bond is rather limited due to the large steric hindrance of the anthracyl moiety, leading to the formation of significant amount of ester **2** (i.e. 24–56%) [10].

On the other hand, neutral aryl palladium complexes are supposed to be formed when operating in the absence of ammonium salt, driving the reaction towards the formation of the intermediate **B**. At this stage, in absence of other evidences, we suggest that interactions between the aromatic ring and the "electron-poor" metallic centre favour the formation of the saturated ester.

In the presence of halide scavengers like silver salts, cationic palladium complexes **C** are formed [24,25]. In that case, it is reasonable to propose a coordination between one of the oxygen atoms of the acetal group and the cationic palladium centre [26]. Such a coordination would restrain the rotation along the $(EtO)_2CH$–CHPd bond, and therefore the H–Pd *syn*-elimination at the acetalic carbon leading to the formation of the expected aldehyde. However, due to the steric hindrance of the aromatic moiety, the rate of the rotation along the ArCH–CHPd bond would be also



Scheme 2. Proposed mechanism involving the different palladium-species to rationalize the selectivity of the arylation of the diethyl acrolein acetal with the 9-bromoanthracene depending on the additives.

restricted as for neutral palladium complexes; therefore the selectivity ester/aldehyde of the reaction would depend on the relative rate of both routes. Such an explanation is supported by the required higher reaction temperature in that case (140 vs. 110 °C) and the influence of water.

In summary, depending on the reaction conditions, anionic, neutral or cationic palladium-species are predominantly formed before the initial determining step of the catalytic cycle. For neutral and cationic palladium-species, specific interactions occur between the palladium centre and the substrate ligands impacting the selectivity of the coupling reaction; no interaction being suggested when considering "electron-rich" anionic species. However, due to the large steric hindrance of the anthracyl group, the H–Pd *syn*-elimination at the benzylic carbon leading to the formation of the unsaturated aldehyde is lowered. As a counterpart, selective synthesis towards the saturated ester is easily achieved while moderate yields towards cinnamaldehyde derivatives are obtained.

Finally, as far as the reaction rate is concerned, both the presence of additives (*n*-Bu_4NOAc, $AgBF_4$, etc.) as well as the nature of the solvent (more or less coordinating) would modify noticeably the electronic character of the active palladium-species (form electron-rich anionic to electron-poor cationic palladium complexes) influencing thus the observed rate of the reaction.

4. Conclusion

While the selective synthesis of 3-aryl propionic ester or 3-arylacrolein through the Heck coupling reaction with various aryl and heteroaryl halides was previously described in the literature, some limitations were found while using the 9-bromoanthracene. In the best cases, equimolar product mixtures were obtained; otherwise by-product formations or dehalogenation were predominant.

In order to find out reaction conditions allowing the selective synthesis of the saturated ester, or of the unsaturated aldehyde, we initiated this study. We showed the reaction conditions influenced drastically the selectivity of the Heck coupling reaction of the 9-bromoanthracene with the acrolein diethyl acetal. Using the $Pd(OAc)_2$ as the catalyst, the ethyl 3-anthracylpropionate was prepared efficiently using only K_2CO_3as the base. On the other hand, the 3-anthracylacrolein was predominantly obtained (i.e. 75%) when working in presence of *n*-Bu_4NOAc using the $Pd(OAc)_2$ or the Herrmann's palladacycle as catalyst [27].

Taking into account all results as well as some reported literature, we proposed mechanisms to explain the different selectivities observed as a dependence on the reaction conditions.

5. Experimental

5.1. General remarks

All manipulations were conducted under inert atmosphere or vacuum conditions using Schlenk techniques including the transfer of the catalysts to the reaction vessel. All glassware was base- and acid-washed and oven dried.

The solvents used for the synthesis of the molecular palladium precursors and catalysts were dried using standard methods. All other chemicals (organic reagents and solvents) were deaerated by an argon flow before they were used. The solvents used for the catalytic experiments are used as received from Aldrich (Chromasolv-plus, water content <0.03% or 0.05% depending on the solvent). The Herrmann's palladacycle was prepared according procedure reported in the literature [19] and store under inert atmosphere until use.

The catalytic reactions were carried out in pressure sealed tubes, under argon. The analysis of the reactants and the products was made by gas chromatography. Conversions and yields were determined by GC.

Liquid NMR spectra were recorded on a BRUKER AC-250 spectrometer. All chemical shifts were measured relative to residual ^1H or ^{13}C NMR resonances in the deuterated solvents: $CDCl_3$, δ 7.25 ppm for ^1H, 77 ppm for ^{13}C.

GC analyses were performed on a HP 4890 chromatograph equipped with a FID detector, a HP 6890 autosampler and a HP-5 column (cross-linked 5% phenyl-methylsiloxane, 30 m × 0.25 mm i.d. × 0.25 μm film thickness). Nitrogen is used as carrier gas.

5.2. Synthesis of the ethyl 3-anthrac-9-ylpropionate

9-Bromoanthracene (2.4 mmol), 3.6 mmol of acrolein diethyl acetal, 3.6 mmol of K_2CO_3 and 2 mol% of $Pd(OAc)_2$ were introduced in a pressure tube under argon. Three millilitres of solvent previously deaerated were added and the mixture was deaerated by an argon flow for 5 min. The reactor was then placed in a pre-heated oil bath at 110 °C for 6–23 h under vigorous stirring and then cooled to room temperature before the reaction mixture was analyzed by GC. At completion of the reaction, the mixture was diluted with 150 mL of HCl 1 N and the resulting mixture was extracted with 4 × 20 mL CH_2Cl_2 or EtOAc. The combined organic layers were washed three times with 15 mL of H_2O, then 15 mL of brine, dried over $MgSO_4$ and evaporated. The residue was then purified by flash chromatography on silica gel. R_f (Petroleum ether (40–60)/ethyl acetate, 4/1) = 0.61. Orange solid, m.p.: 162 °C. IR (KBr): 1728, 1184 cm^{-1}. NMR ^1H (250 MHz, $CDCl_3$): 8.35 (s, 1H,Cq–C*H*–Cq); 8.32 (d, $^3J_{H-H}$ = 8.8 Hz, 2H, Cq–C*H*=CH); 8.01 (d, $^3J_{H-H}$ = 8.2 Hz, 2H, Cq–C*H*=CH); 7.46–7.60 (massif, 4H, Cq–CH=C*H*); 4.26 (q, $^3J_{H-H}$ = 7.1 Hz, 2H,COO*CH*$_2$CH$_3$); 4.01 (m, 2H, Ant-CH$_2$*CH*$_2$COOEt); 2.82 (m, 2H, Ant-*CH*$_2$CH$_2$COOEt); 1.32 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, COOCH$_2$*CH*$_3$). NMR ^{13}C (62.9 MHz, $CDCl_3$): 173.13 (*C*OOEt); 132.50 (C^9–$C_{14}H_9$); 131.62 (C^{13} + C^{14}–$C_{14}H_9$); 129.53 (C^{11}–$C_{14}H_9$); 129.36 (C^{12}–$C_{14}H_9$); 126.41 (C^1 + C^8–$C_{14}H_9$); 125.93 (C^2 + C^7–$C_{14}H_9$); 124.95 (C^3 + C^6–$C_{14}H_9$); 123.97(C^{10}–$C_{14}H_9$); 60.68 (COO*C*H$_2$); 35.41 (Ant-*C*H$_2$COOEt); 23.35 (Ant-*C*H$_2$CH$_2$COOEt); 14.29 (COOCH$_2$*C*H$_3$).$C_{19}H_{18}O_2$: 278.13 g mol^{-1}. MS: *m*/*z* (%) = 278 (67) [$M^{+\cdot}$], 191 (100) [M−$CH_2COOC_2H_5$]. HRMS calc. for $C_{19}H_{18}O_2$ [$M^{+\cdot}$]: 278.1307, found: 278.1303. Anal. Calc. for $C_{19}H_{18}O_2$ (278.35): H, 6.52; C, 81.99. Found: H, 6.45; C, 81.73%.

5.3. Synthesis of the 3-anthrac-9-ylpropenal

9-Bromo anthracene (2.4 mmol), 3.6 mmol of acrolein diethyl acetal, 3.6 mmol of K_2CO_3, 4.8 mmol of *n*-Bu_4NOAc and 2 mol% of $Pd(OAc)_2$ were introduced in a pressure tube under argon. Three millilitres of solvent DMF previously deaerated were added and the mixture was deaerated by an argon flow for 5 min. The reactor was then placed in a pre-heated oil bath at 110 °C for 6–24 h under vigorous stirring and then cooled to room temperature before the reaction mixture was analyzed by GC. The same procedure as described before was used for extraction and purification. R_f (petroleum-ether (40–60)/ethyl acetate, 9/1) = 0.45. Yellow solid m.p.: 166 °C. IR (KBr): 1670, 1127 cm^{-1}. NMR ^1H (250 MHz,$CDCl_3$): 9.96 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, Ant-CH=CH–C*H*O); 8.46 (s, 1H); 8.45 (d, $^3J_{H-H}$ = 16.3 Hz, 1H, Ant-C*H*=CH–CHO); 8.14 (m, 2H, Cq–C*H*=CH); 7.968 (m, 2H, Cq–C*H*=CH); 7.52–7.42 (m, 4H, Cq–CH=C*H*); 6.71 (dd, $^3J_{H-H}$ = 16.3 Hz, $^3J_{H-H}$ = 7.8 Hz, 1H, Ant-CH=C*H*–CHO). NMR ^{13}C (62.9 MHz, $CDCl_3$): 193.50 (*C*HO); 149.95 (HC=CH–CHO); 137.47 (C^9–$C_{14}H_9$); 131.20 (C^{13} + C^{14}–$C_{14}H_9$); 129.42 (C^{11}–$C_{14}H_9$); 129.13 (C^{12}–$C_{14}H_9$); 129.06 (C^1–$C_{14}H_9$); 128.19 (C^8–$C_{14}H_9$); 126.87 (C^2 + C^7–$C_{14}H_9$); 125.53 (C^3 + C^6–$C_{14}H_9$); 124.69 (C^{10}–$C_{14}H_9$). $C_{17}H_{12}O$: 232.09 g mol^{-1}. MS: *m*/*z* (%) = 232 (77) [$M^{+\cdot}$], 203 (100) [$M^{+\cdot}$−CO], 178. HRMS calc. for $C_{17}H_{12}O$ [$MH^{+\cdot}$]:

233.0966, found: 233.0965. Anal. Calc. for $C_{17}H_{12}O$ (232.09): H, 5.21; C, 87.90. Found: H, 5.09; C, 87.64%.

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