Acryloxy and Methacryloxy Palladation of Alkenes

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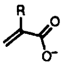
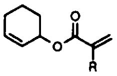
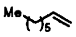
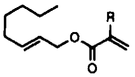
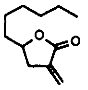
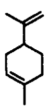
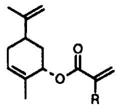
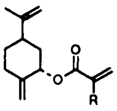
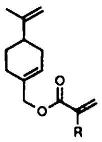
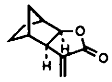
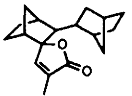
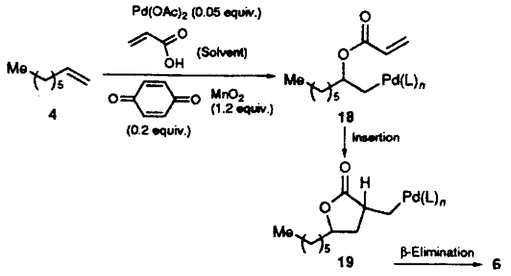
Acrylic and methacrylic esters can be obtained in one step from alkenes using a Pd(OAc)$_2$/benzoquinone/MnO$_2$ catalyst; with acrylic acid and a suitable alkene, it is also possible to obtain α-methylene γ-lactones in one step.

The scope and limitations of palladium-catalysed allylic acetoxylation of alkenes have been extensively studied, especially from the mechanistic point of view.[1] The formation of η^3-allylpalladium complexes competes with 1,2-acetoxypalladation[2] depending on the alkene structure, and also on the nature of the catalytic system. Although the chemical behaviour of a great variety of such catalysts has been tested,[3] two of them are characteristic and typical: (*i*) the classical Wacker system PdCl$_2$/CuCl$_2$/O$_2$ which favours 1,2-addition with the formation of chlorinated derivatives; (*ii*) the Pd(OAc)$_2$/benzoquinone/MnO$_2$ mixture which favours the formation of intermediate π-allyl complexes. The latter are probably stabilized by the presence of the quinone, which not only acts as a redox partner in the catalytic system, but also acts as a ligand.[4] The stabilization of such an intermediate π-allyl complex can also be observed when a second double bond is present in the alkene, as in vinylcyclohexene or limonene.[2,5]

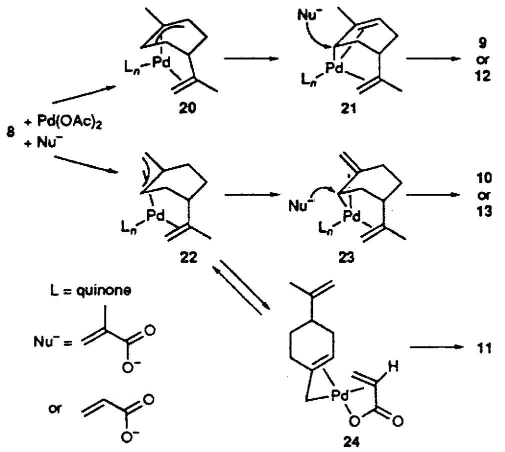
We wondered if a double bond belonging to the nucleophile could play a similar role in such a way as to favour the intermediacy of a π-allyl complex. It was therefore of interest to study the reactivity of acrylates and methacrylates which, in contrast to the acetate anion, are vinylogous nucleophiles. We report here the results which we have observed for acryloxy- and methacryloxy-palladation of four alkenes[6] (Table 1) using the Pd(OAc)$_2$/benzoquinone/MnO$_2$ catalyst.† Their chemical behaviour is representative of cyclic **1**, linear **4**, bridged bicyclic monoalkene **15**, as well as of a non-conjugated dialkene **8**. The yields are relatively low because of the ease with which the acrylates polymerise.‡ The formation of allylic acrylate **2**§ and methacrylate **3** from cyclohexene **1** (entries 1 and 2, Table 1) parallels the formation of allylic acetates previously observed.[1] This behaviour, which does not depend on the ring size,[7] is a good indication that a π-allyl intermediate is involved.[8] This reaction, which had been previously observed with propene and 2-methylpropene,[9] is of practical interest because the formation of acrylates and methacrylates from alkenes is generally done *via* the corresponding alcohols, which are further esterified or transesterified; the latter reaction requires mild catalysts such as distannoxanes[10] because of the acrylate reactivity. With oct-1-ene **4** (entry 3), allylic acrylation is also observed, but the α-methylene γ-lactone **6** is the major product of the reaction. The formation of this kind of derivative is of synthetic interest[11] because a carboxylation step is generally required.[12] This reaction also provides interesting information about the acryloxypalladation mechanism. With a terminal alkene such as **4**, 1,2-Markovnikov addition of the acrylate which yields **18** (Scheme 1) competes efficiently with the π-allyl complex formation. As soon as σ-complex **18** is obtained, the double bond of the acrylate inserts into the carbon–palladium bond to form **19**, which undergoes β-elimination to yield **6**. As the latter process cannot occur when methacrylic acid is used, allylic methacryloxypalladation is the only process observed with **4** (entry 4), which yields **7**. With norbornene **15** (entry 7), the lack of

Table 1 Acryloxy- and methacryloxy-palladation of typical alkenes and dialkenes with the Pd(OAc)$_2$/quinone/MnO$_2$ catalyst

Entry	Alkene	R 	T/°C	Reaction time/h	Yield (%)	Products (ratio)
1	 **1**	H	60	72	55	 **2** R = H
2	**1**	Me	60	72	45	**3** R = Me
3	 **4**	H	75	72	40	 **5** R = H 
4	**4**	Me	75	48	70	**7** R = Me **6** (1 : 4)
5	 **8**	H	25	72	40	 **9**  **10**  **11** R = H (3 : 2 : 5)
6	**8**	Me	30	72	36	**12** **13** **14** R = Me (1 : 1 : 0)
7	 **15**	H	80	72	40	 **16**
8	**15**	Me	90	72	35	 **17**



Scheme 1 Formation of the α-methylene lactone **6** from oct-1-ene *via* intermediate **18** resulting from the 1,2-Markovnikov addition to the double bond



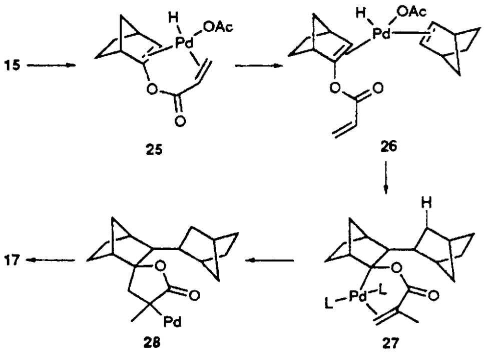
Scheme 2 Acryloxypalladation and methacryloxypalladation of limonene

reactivity of the bridgehead hydrogens forbids the formation of a π-allyl intermediate; it is therefore no surprise that **16** is now the exclusive product of the acryloxypalladation.[13]

The formation of acrylate **9** and methacrylate **12** from limonene **8** (entries 5 and 6) involves a π-allyl intermediate **20** (Scheme 2) and the corresponding σ–π-complex **21** which undergoes the nucleophilic attack, as was the case for the formation of the corresponding acetate[2,5] (entries 5 and 6). But in the present case, the formation of π-allyl complex **22** can also be taken into consideration; nucleophilic attack on the corresponding π–σ-structure **23**, yields either **10** or **13** (entries 5 and 6). Furthermore, when the acrylate anion enters the coordination sphere of palladium in **22**, it is possible to form the σ–π-complex **24**, which is now stabilized by the acrylate double bond; further reductive elimination yields acrylate **11**. The latter reaction does occur with the methacrylate, either because it is more hindered, or more probably because it is more nucleophilic, so that only external attack occurs on either **21** or **23**.¶

As mentioned earlier, α-methylene γ-lactone **16** is the unique product resulting from acryloxypalladation of norbornene **15** (entry 7).[6,13] But when methacrylic acid is used instead, the final β-elimination step (see Scheme 1) can no longer occur, because the methyl group has replaced the hydrogen which previously underwent β-elimination. A new unsaturated lactone **17** is then produced (entry 8). Although the mechanistic rationalisation of this result is difficult, it is possible to suggest the formation of an intermediate bis(π-complex) **25** resulting from methacryloxypalladation of the norbornene double bond, followed by β-elimination (Scheme 3). Ligand exchange between the methacrylate double bond and norbornene yields **26**, which after a double insertion gives rise to **27**. Further insertion of the methacrylate double bond into the carbon–palladium bond gives **28**, which after β-elimination yields **17**.

In conclusion, it is possible to say that 1,2-addition resulting



Scheme 3 Formation of α,β-unsaturated lactone **17** by methacryloxypalladation of norbornene **15**

from the acryloxy- or methacryloxy-palladation of isolated double bonds provides an entry into α-methylene γ-lactones. Depending on the structure of the alkenes, this reaction competes efficiently with the π-allyl intermediate formation, giving raise to allylic acrylates or methacrylates. The perspectives offered by this versatile reaction are currently under intensive investigation in our laboratories.

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Footnotes

† This catalyst was preferred to the classical Wacker catalyst because the latter generally gives poor yields and complex mixtures which essentially contain chlorinated acrylates resulting from a 1,2-addition.

‡ The acrylic and methacrylic acids also contain appreciable amounts of dimers which are difficult to control; these apparently depend on the time the acids have been stored.

§ All products reported in this paper have been isolated, purified and characterized by IR, ^{1}H and ^{13}C NMR and gave satisfactory elemental analyses.

¶ It must be pointed out that the equilibrium shown in Scheme 2 is most likely to be favoured by the quinone ligand. Indeed, with the classical Wacker catalyst ($PdCl_2/CuCl_2$), acrylate **9** and methacrylate **12** are the exclusive products of the reaction.

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