Evidence for the Intermediacy of (η^3-Allyl)palladium Complexes in the Palladium-Catalyzed Acryloxylation of Cycloalkenes: Unexpected Oxidation of 1,5-Cyclooctadiene

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Palladium-catalyzed acryloxylation of several cycloalkenes in the presence of the $Pd(OAc)_2$/*p*-benzoquinone/MnO_2 catalytic system is reported. This oxidation reaction yields allylic acrylates as the sole products through the intermediacy of an η^3-allyl complex. However, with 1,5-cyclooctadiene (**3**), cyclooct-4-enone (**4**) is the major reaction product. Its formation results from oxidation, which is also observed in the palladium-catalyzed acetoxylation of **3**. It has been shown that this is the result of a 1,2-*trans* addition (acryloxy-palladation), followed by a β-hydride elimination, which yields an enol acrylate or acetate. A second Markovnikov-oriented 1,2-*trans*-acryloxy-palladation on the latter yields a palladium complex, rearrangement of which gives **4**.

The mechanism of palladium-catalyzed allylic acetoxylation is a subject of current interest.[1] Using 1,2-dideuteriocyclohexene, evidence has recently been provided in an elegant manner for the intermediacy of an (η^3-allyl)palladium species in the quinone-based palladium-catalyzed allylic acetoxylation of cyclohexene. A second mechanism has been suggested for the palladium-catalyzed allylic oxidation of olefins, which can also proceed via a (σ-alkyl)palladium complex resulting from a 1,2-addition reaction.

These two processes can easily be differentiated from the parent palladium-catalyzed acryloxylation reaction.[2] *cis*-1,2-Addition of the acrylate nucleophile and palladium to a double bond yields an α-methylene-γ-butyrolactone, provided that the acrylate double bond can undergo insertion into the carbon−palladium bond formed after the initial addition reaction. This is the case for norbornene (Figure 1), where no (η^3-allyl)palladium complex can form,[2a] so that only formation of the lactone is observed (40% isolated yield; yields are generally rather low because of the ease with which acrylates polymerize).

With oct-1-ene, however, (η^3-allyl)palladium complex formation competes with the 1,2-addition, so that formation of both the lactone and of allylic acrylates (4:1 ratio) is observed (40% overall isolated yield).

As α-methylene-γ-butyrolactones are present in a great number of natural products,[3] it was of interest to study the scope of the palladium-catalyzed acryloxylation of cycloalkenes in the hope of finding appropriate conditions that would favour the exclusive formation of α-methylene-γ-butyrolactones.

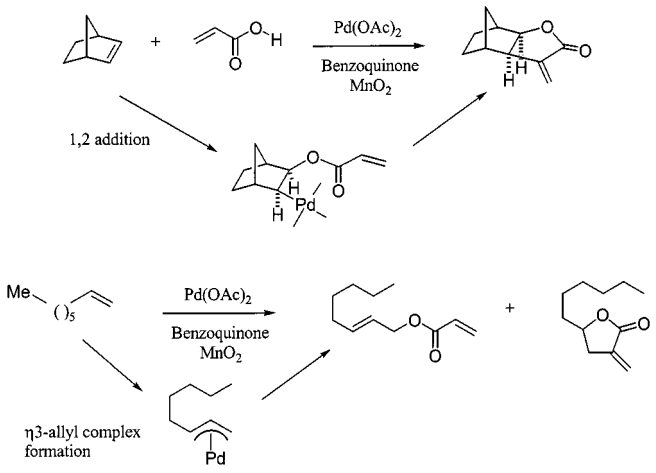

Figure 1

According to modelling studies,[4] the formation of η^3-allyl complexes is very sensitive to the valence and dihedral angle values in the allylic framework, so that the mechanism proceeding via η^3-allyl intermediates should be preferred over the alternative 1,2-oxypalladation pathway.[2a] This was a good reason to study the acryloxylation of cycloalkenes **1a−d** with different ring sizes. Use of these substrates was also anticipated to permit comparison of the behavior of acetate and acrylate as nucleophiles in the palladium-catalyzed acetoxylation and acryloxylation.[2][5] Moreover, such a study was expected to allow a comparison with results obtained for the catalytic acryloxylation of vinyl cycloalkanes and *exo*-methylenecycloalkanes, where the ratio of α-methylene-γ-butyrolactones to allylic acrylates was found to be ring-size-dependent.[2]

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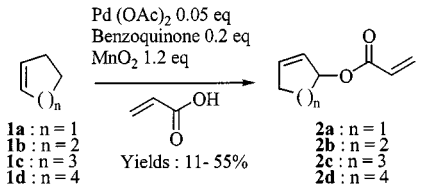
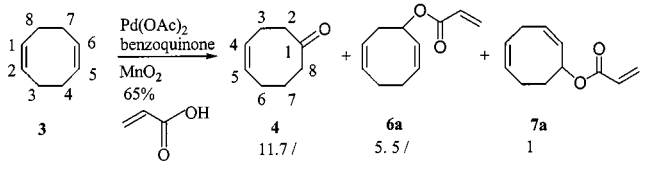


Scheme 1. Palladium-catalyzed acryloxylation of cycloalkenes

As can be seen in Scheme 1, only the formation of allylic acrylates **2a−d** is observed, although the isolated yields are lower than those seen for the allylic acetates formed in the corresponding acetoxylation reactions.[5] As neither vinylic acrylates nor α-methylene-γ-butyrolactones are observed, this process must involve an intermediate η^3-allyl complex. Under these experimental conditions, cyclic alkenes **1a−d** form a η^3-allyl complex much more easily than they undergo an acrylate 1,2-addition to the double bond.[2]

One way of modifying both the structure of the remainder of the skeleton and the reactivity of the cycloalkene double bond is to introduce a second double bond in the ring, which might possibly participate as a spectator ligand in the 1,2-acryloxypalladation of the first double bond. Clearly, 1,5-cyclooctadiene (**3**) was the ideal candidate for such a study (see below); it was therefore submitted to palladium-catalyzed acryloxylation with the expectation that the presence of a second double bond in the ring would modify the outcome of the acryloxylation reaction by competing with the acrylate double bond insertion. The result was, however, completely unexpected as neither an allylic acrylate nor an α-methylene-γ-butyrolactone was formed as the major product. Instead, with catalytic amounts of palladium, the acryloxylation of 1,5-cyclooctadiene (**3**) led to formation of three products (total isolated yield of 65%) (Scheme 2). The two major products were cyclooct-4-enone (**4**) (selectivity = 64.5%) and allylic acrylate **6a** (selectivity = 30%), which were accompanied by a small amount of allylic acrylate **7a** (selectivity = 5.5%). Acetoxylation of 1,5-cyclooctadiene (**3**), carried out under the same experimental conditions, yielded cyclooct-4-enone (**4**) as the sole reaction product (47% yield).

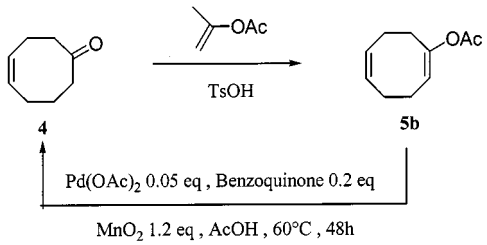


Scheme 2. Palladium-catalyzed acryloxylation of 1,5-cyclooctadiene (**3**)

Thus, the presence of the second double bond in 1,5-cyclooctadiene (**3**) does indeed modify the course of the acryloxylation reaction, by forcing the 1,2-addition to occur exclusively in a *trans* fashion. The resulting 1,2-*trans* adduct can be stabilized by π-complexation with the unchanged double bond of diene **3** in the tub conformation.[6] In the presence of stoichiometric amounts of palladium and suitable counterions, such (σ-η^2)-Pd^{II} complexes have in fact been isolated and characterized.[7] In the case of the related 1,4-cyclohexadiene, it has also been shown that palladium acetate reacts by 1,2-*trans* addition.[8]

In earlier work,[9] one of us made the observation that cyclooct-4-enone (**4**) was obtained by oxidation of 1,5-cyclooctadiene (**3**) in the presence of palladium acetate, using hydrogen peroxide in acetic acid. The formation of the enone was then attributed to the presence of hydrogen peroxide. However, when these experiments were repeated using only hydrogen peroxide, without acetic acid, the yield of enone **4** dropped from 42% to just 6%.[9] This gave an indication that the formation of **4** requires the presence of acetic acid, and is probably not due to the use of hydrogen peroxide as the oxidizing species. The small amount of enone **4** observed in absence of acetic acid might be the result of a hydroxypalladation.[10] The enone **4** also remains the major product in the acryloxylation reaction (or acetoxylation reaction) in the absence of hydrogen peroxide.

Indeed, treatment of independently synthesized **5b** with palladium acetate, benzoquinone, and manganese dioxide in acetic acid yields **4** (50% yield with 50% conversion) as expected (Scheme 3).[11]



Scheme 3. Synthesis and reaction of the intermediate **5b**

Palladium-catalyzed *trans*-acetoxylation or -acryloxylation of **3** yields complex **B** (Scheme 4), which is derived from the di-η^2 complex **A** formed in the presence of **3** and benzoquinone. An NMR-spectroscopic investigation of a series of (σ-η^2)-palladium(II) complexes originating from 1,5-cyclooctadiene−Pd^0−benzoquinone complexes has shown that the 1,2-addition of the heteroatomic nucleophile and palladium does indeed occur with *trans* stereochemistry.[7] This was also found to be the case for the acryloxypalladation.[13] Therefore, initial 1,2-*trans* addition of the nucleophile to **3** yields complex **B**; a *cis*-β-hydride elimination reaction then gives the di-η^2 complex **C**. A Markovnikov-type attack of another acetate (or acrylate) on **C** gives rise to a diacetate-substituted palladium σ-complex **D**, formation of which is favored by the stabilization of the thus formed C−Pd bond by the second double bond of the cyclooctadiene derivative. Complex **D** then undergoes the rearrangement discussed by Schultz and Rony[12] to give the σ-complex **E**, which yields **4** after reductive elimination. Trideuterioacetic anhydride **8**, which results from the decomposition of **D** according to Schultz and Rony′s mechanism, could indeed be detected by NMR when **5b** was treated with tetradeuterioacetic acid in the presence of the usual palladium-catalytic system.

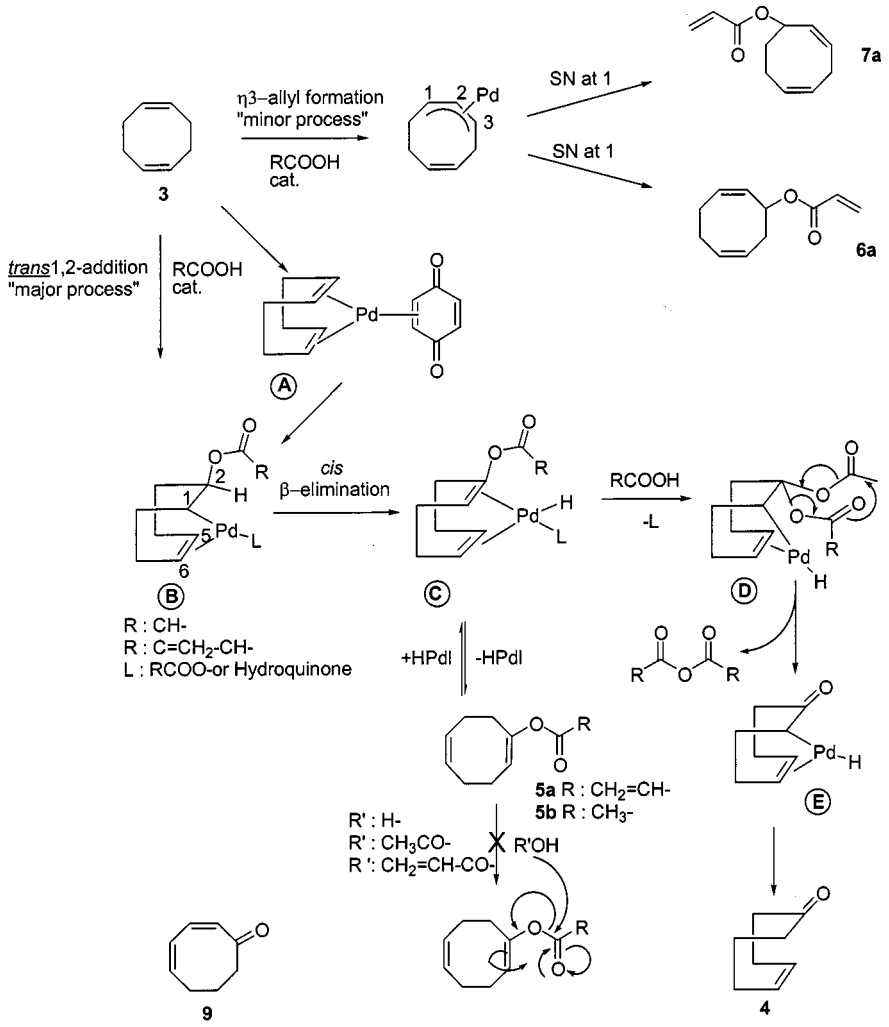
Another outcome of complex **C** could be a reversible decomplexation to yield enol esters **5a** or **5b**. The latter could

indeed be detected in the reaction mixture following palladium-catalyzed acetoxylation of **3**. Furthermore, treatment of independently synthesized[15] **5b** with palladium acetate, benzoquinone, and manganese dioxide in acetic acid yielded enone **4** (50% yield with 50% conversion) via **C**, **D** and **E** as expected. It is noteworthy that an additional product could be detected in the reaction mixture, namely 2,4-cyclooctadienone **9**. This compound was most probably formed by isomerization of **5b** with subsequent oxidative degradation.[15]

A question that arises is why the enol ester **5b** does not undergo hydrolysis directly to the enone **4**. When the usual reaction mixture [1,5-cyclooctadiene (**3**), palladium acetate, benzoquinone, manganese dioxide, acrylic acid] was treated with deuterium oxide for three days, the ketone **4** obtained was found not to be deuterated. It therefore seems unlikely that enol acetate **5b** present in the reaction medium (see above) is directly deuteriolyzed (or hydrolyzed) to enone **4**. Moreover, treatment of ketone **4** under similarly acidic conditions does not lead to deuteration; basic conditions are required to deuterate this ketone.

As a consequence, the most reasonable pathway from **3** to **4** is that proceeding via **A**, **B**, **C**, **D**, and **E**, with the likelihood that **C** is in equilibrium with **5**. It is clear from the above discussion that the formation of **4**, **6a**, and **7a** from **3** shows that the 1,2-*trans* addition and formation of the more common (η^3-allyl)palladium intermediate occur concurrently, with the former process predominating.

In conclusion, the present work shows that the acryloxylation reaction of cyclic monoalkenes **1a–d** (five- to eight-membered rings) proceeds preferentially according to a mechanism involving an (η^3-allyl)palladium intermediate, to yield exclusively the allylic acrylates **2a–d**. The overall structure of the intracyclic double bond and the presence of suitably located allylic hydrogen atoms favors the intermediacy of an (η^3-allyl)palladium complex as opposed to the *cis*-1,2 addition process, which would give rise to the α-methylene-γ-butyrolactone. However, in the presence of a second suitably located double bond,[4] as in 1,5-cyclooctadiene (**3**), we have shown that a competing *trans*-1,2-acryloxypalladation addition process is preferred, yielding enone **4** by the mechanism previously delineated by Schultz and Rony.[12] Incidentally, this pathway provides a more efficient access to the enone **4**, which is obtained in an overall yield of 42–47% (in a one-step synthesis) compared with the 27% previously reported from a multi-step synthesis.[14]



Scheme 4. Mechanism of formation of enone **4** from **3**

The formation of α-methylene-γ-butyrolactones is not observed in the acryloxypalladation of cyclic monoalkenes, in contrast to the case of *exo*-methylenecycloalkanes and vinylcycloalkanes.[2b] In order to obtain the lactone, the initial acryloxypalladation would have had to have occurred with *cis* stereochemistry, as was previously observed in the case of norbornene.[2a] We are currently carrying out further investigations into the reactivity of nonconjugated dienes with emphasis on delineating the influence of the second double bond on the 1,2-addition process at the first as a function of its relative location and stereochemistry.

Experimental Section

General: Chemicals were generally purchased from Aldrich and were used as received. Acrylic acid was donated by ELF-ATOCHEM. The percentage of dimer in the latter was assayed by NMR (< 3%). − Thin-layer chromatography (TLC) was carried out on aluminium-backed sheets precoated with Merck silica gel 60 F_{254}. The spots were visualized with UV light or developed with *para*-anisaldehyde/H_2SO_4/AcOH in EtOH. − Column chromatography was carried out on Merck silica gel, 60−230 mesh. − Microanalyses were performed by the University of Marseille Microanalytical Service. − IR: Perkin−Elmer spectrometer; samples in $CHCl_3$ solution, frequencies are reported in cm^{-1}. − UV: Philips PU 8720 UV/Vis; wavelengths are reported in nm. − NMR: Gemini 200, Gemini 300; for ^1H and ^{13}C NMR, $CDCl_3$ as solvent, TMS as internal standard; shifts are reported in ppm relative to TMS, couplings are given in Hz. − All yields quoted refer to isolated and purified products.

General Procedure for the Palladium-Catalyzed Acryloxylation: $Pd(OAc)_2$ (0.112 g, 0.5 mmol), *p*-benzoquinone (0.216 g, 2 mmol), MnO_2 (1.044 g, 12 mmol), and acrylic acid (25 mL) were placed in a 100-mL two-necked round-bottomed flask fitted with a reflux condenser. The resulting suspension was stirred for 30 min at room temperature and then the alkene (10 mmol) was added. The reaction mixture was heated to the requisite temperature and the progress of the reaction was monitored by TLC. Once the reaction had reached completion, the mixture was cooled to room temperature and 20 mL of a 1:1 mixture of pentane/diethyl ether was added. The resulting solution was stirred for 30 min, filtered through wet Celite (C 545), and the Celite was washed with water (3 × 20 mL) and diethyl ether (2 × 25 mL). The combined organic phases were carefully washed, first with saturated Na_2CO_3 solution until neutral, then with brine. The pH was then adjusted to 7. The organic phase was dried with $MgSO_4$, filtered through wet Celite (C 545), and concentrated to dryness under reduced pressure without heating. The reaction products were then isolated by column chromatography on silica, eluting with various solvents or solvent mixtures increasing in polarity. All samples were isolated as liquids.

Cyclopent-2-enyl Acrylate (2a): Prepared from 0.68 g (10 mmol) of cyclopentene (**1a**) according to the general procedure for palladium-catalyzed acryloxylation by heating at 50°C for 36 h; yield 11%. − ^1H NMR (200 MHz, $CDCl_3$): δ = 6.5 (dd, $J_{8c,8t}$ = 1.6 Hz, $J_{7,8t}$ = 16 Hz, 1 H, H^{8t}), 6.15 (dd, $J_{7,8c}$ = 10 Hz, $J_{7,8t}$ = 16 Hz, 1 H, H^7), 6.1 (m, 1 H, H^2), 5.95 (dd, $J_{8c,8t}$ = 1.6 Hz, $J_{7,8c}$ = 10 Hz, 1 H, H^{8c}), 5.85 (m, 1 H, H^3), 5.80 (m, 1 H, H^1), 2.3−1.7 (m, 4 H, H^4 and H^5). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 165.0 (q, C^6), 133.9 (t, C^2), 132.2 (s, C^8), 130.9 (t, C^7), 128.4 (t, C^3), 78.1 (t, C^1), 26.9 (s, C^4), 23.1 (s, C^5). − IR ($CHCl_3$): $\tilde{\nu}$ = 3120 (C=CH), 2910 (CH_2), 2840 (CH_2), 1720 (C=O), 1650 (C=C conj.), 1610 (C=C aliph.), 1460 (CH_2), 1290 (CH_2), 1260 (C=O), 1190 (C=C), 1040 (C=C), 980 (CH_2), 910 (CH_2), 810 (CH_2). − $C_8H_{10}O_2$ (138.16): calcd. C 69.55, H 7.29; found C 69.51, H 7.40.

Cyclohex-2-enyl Acrylate (2b): Prepared from 0.82 g (10 mmol) of cyclohexene (**1b**) according to the general procedure for palladium-catalyzed acryloxylation by heating at 60°C for 72 h; yield 55% (75% conversion). − ^1H NMR (200 MHz, $CDCl_3$): δ = 6.4 (dd, $J_{9c,9t}$ = 1.7 Hz, $J_{8,9t}$ = 16.5 Hz, 1 H, H^{9t}), 6.05 (dd, $J_{8,9c}$ = 10.2 Hz, $J_{8,9t}$ = 16.5 Hz, 1 H, H^8), 5.9 (m, 1 H, H^2), 5.75 (dd, $J_{9c,9t}$ = 1.7 Hz, $J_{8,9c}$ = 10.2 Hz, 1 H, H^{9c}), 5.7 (m, 1 H, H^3), 5.3 (m, 1 H, H^1), 2.3−1.5 (m, 6 H, H^4, H^5 and H^6). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 165.6 (q, C^7), 132.5 (t, C^2), 130.1 (s, C^9), 128.7 (t, C^8), 125.3 (t, C^3), 67.9 (t, C^1), 28.0 (s, C^6), 24.5 (s, C^4), 18.6 (s, C^5). − IR ($CHCl_3$): $\tilde{\nu}$ = 3120 (C=CH), 2940 (CH_2), 2860 (CH_2), 2820 (CH_2), 1720 (C=O), 1630 (C=C conj.), 1610 (C=C aliph.), 1400 (CH_2), 1290 (CH_2), 1260 (C-O), 1190 (C-C). − $C_9H_{12}O_2$ (152.19): calcd. C 71.02, H 7.94; found C 70.99, H 8.06.

Cyclohept-2-enyl Acrylate (2c): Prepared from 0.96 g (10 mmol) of cycloheptene (**1c**) according to the general procedure for palladium-catalyzed acryloxylation by heating at 60°C for 41 h; yield 21% (60% conversion). − ^1H NMR (200 MHz, $CDCl_3$): δ = 6.35 (dd, $J_{10c,10t}$ = 1.7 Hz, $J_{9,10t}$ = 13.0 Hz, 1 H, H^{10t}), 6.05 (dd, $J_{9,10c}$ = 10.0 Hz, $J_{9,10t}$ = 13.0 Hz, 1 H, H^9), 5.8 (m, 1 H, H^2), 5.75 (dd, $J_{10c,10t}$ = 1.7 Hz, $J_{9,10c}$ = 10.0 Hz, 1 H, H^{10c}), 5.60 (m, 1 H, H^3), 5.42 (m, 1 H, H^1), 2.2−1.5 (m, 8 H, H^4, H^5, H^6 and H^7). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 165.8 (q, C^8), 133.9 (t, C^2), 132.0 (s, C^9), 130.7 (t, C^{10}), 129.3 (t, C^3), 66.2 (t, C^1), 33.1 (s, C^7), 28.8 (s, C^4), 26.9 (s, C^5 and C^6). − IR ($CHCl_3$): $\tilde{\nu}$ = 3120 (C=CH), 2930 (CH_2), 2840 (CH_2), 1720 (C=O), 1640 (C=C conj.), 1610 (C=C aliph.), 1460 (CH_2), 1290 (CH_2), 1260 (C-O), 1190 (C-C), 1040 (C-C), 980 (CH_2). − $C_{10}H_{14}O_2$ (166.24): calcd. C 72.26, H 8.49; found C 72.19, H 8.62.

Cyclooct-2-enyl Acrylate (2d): Prepared from 1.10 g (10 mmol) of cyclooctene (**1d**) according to the general procedure for palladium-catalyzed acryloxylation by heating at 60°C for 96 h; yield 11% (20% conversion). − ^1H NMR (200 MHz, $CDCl_3$): δ = 6.6 (dd, $J_{11c,11t}$ = 1.5 Hz, $J_{10,11t}$ = 17.0 Hz, 1 H, H^{11t}), 6.35 (dd, $J_{10,11c}$ = 10 Hz, $J_{10,11t}$ = 17.0 Hz, 1 H, H^{10}), 6.05 (dd, $J_{11c,11t}$ = 1.5 Hz, $J_{10,11c}$ = 10.0 Hz, 1 H, H^{11c}), 5.9 (m, 1 H, H^2), 5.8 (m, 1 H, H^3), 5.75 (m, 1 H, H^1), 2.3−1.3 (m, 10 H, H^4, H^5, H^6, H^7 and H^8). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 170.8 (q, C^9), 133.3 (s, C^{11}), 128.3 (t, C^2 and C^{10}), 117.5 (t, C^3), 66.0 (t, C^1), 35.1 (s, C^8), 32.0 (s, C^4), 27.2 (s, C^5), 23.0 (s, C^6), 17.3 (s, C^7). − IR ($CHCl_3$): $\tilde{\nu}$ = 3100 (C=CH), 2950 (CH_2), 2890 (CH_2), 1710 (C=O), 1630 (C=C conj.), 1610 (C=C aliph.), 1500 (CH_2), 1290 (CH_2), 1270 (C-O), 1175 (C-C). − $C_{11}H_{16}O_2$ (180.25): calcd. C 73.30, H 8.95; found C 73.41, H 9.07.

Acryloxylation of 1,5-Cyclooctadiene (3): This reaction was performed according to the general procedure for palladium-catalyzed acryloxylation using 1.08 g (10 mmol) of 1,5-cyclooctadiene **3** and heating at 60°C for 72 h (100% conversion). Three products (**6a**, **7a**, **4**) were isolated by column chromatography (70−230 mesh SiO_2) eluting with a pentane/diethyl ether gradient.

Allylic Acrylates (6a and 7a): Yield: 0.405 g (23%). − GC: 85:15, R_f = 0.8 (pentane/diethyl ether, 1:1). − IR ($CHCl_3$): $\tilde{\nu}$ = 3050 (C=CH), 2950 (CH_2), 2900 (CH_2), 2840 (CH_2), 1720 (C=O), 1660 (C=C conj.), 1630 (C=C aliph.), 1450 (CH_2), 1300 (CH_2), 1280 (C-O), 1200 (C-C). − $C_{11}H_{14}O_2$ (178.23): calcd. C 74.13, H 7.92; found C 74.07, H 7.87. − **6a:** ^1H NMR (200 MHz, $CDCl_3$): δ = 6.4 (dd, $J_{11c,11t}$ = 1.6 Hz, $J_{10,11t}$ = 16.7 Hz, 1 H, H^{11t}), 6.1 (m, 1 H, H^{10}), 5.80 (dd, $J_{11c,11t}$ = 1.6 Hz, $J_{10,11c}$ = 16.7 Hz, 1 H, H^{11t}), 5.3 (m, 1 H, H^1), 2.9 (d, 2 H), 2.7−1.2 (m, 4 H). − ^{13}C NMR (50.3 MHz,

$CDCl_3$): δ = 165.3 (q, C^9), 130.1 (s, C^{11}), 129.4 (t, C^{10}), 128.7−128.6 (t, C^3, C^2, C^6 and C^7), 72.5 (t, C^1), 29.1 (s, C^4), 28.5 (s, C^5), 22.9 (s, C^8). − **7a:** ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.4 (dd, $J_{11c,11t}$ = 1.6 Hz, $J_{10,11t}$ = 16.7 Hz, 1 H, H^{11t}), 6.1 (m, 1 H, H^{10}), 5.80 (dd, $J_{11c,11t}$ = 1.6 Hz, $J_{10,11c}$ = 16.7 Hz, 1 H, H^{11t}), 5.05 (m, 1 H, H^1), 2.9 (d, 2 H), 2.7−1.2 (m, 4 H). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 165.3 (q, C^9), 130.1 (s, C^{11}), 129.4 (t, C^{10}), 128.7−128.6 (t, C^2, C^3, C^5 and C^6), 72.3 (t, C^1), 31.9 (s, C^4), 27.0 (s, C^7), 11.9 (s, C^8).

Cyclooct-4-enone (4): Yield: 0.521 g (42%); R_f = 0.42 (pentane/diethyl ether, 1:1). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.7 (m, 2 H), 2.45 (m, 6 H), 2.15 (m, 2 H), 1.65 (m, 2 H). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 215.0 (q, C^1), 130.4−130.0 (t, C^4 and C^5), 46.9 (s, C^8), 40.0 (s, C^2), 26.0 (s, C^6), 23.6 (s, C^3), 21.5 (s, C^7). − IR ($CHCl_3$): $\tilde{\nu}$ = 3020 (C=C−H), 2950 (CH_2), 2860 (CH_2), 1700 (C=O), 1650 (C=C), 1460 (CH_2), 1440 (CH_2), 1360 (CH_2), 1220 (C−O), 880 (CH_2), 720 (CH_2). − UV ($CHCl_3$): λ_{max} (lg ε) = 244.9 nm (2.12). − $C_8H_{12}O$ (124.18): calcd. C 77.37, H 9.73; found C 77.60, H 9.24.

Acryloxylation of 1,5-Cyclooctadiene (3) with D_2O Quenching: The reaction was performed according to the general procedure for palladium-catalyzed acryloxylation by heating 0.108 g of 1,5-cyclooctadiene (**3**), 0.112 g of $Pd(OAc)_2$, 0.216 g of benzoquinone, 1.044 g of MnO_2, and 25 mL of acrylic acid at 60°C for 72 h. Deuterium oxide (3 mL) was then added to the reaction mixture, which was worked-up in the usual manner to afford cyclooct-4-enone (**4**) (0.50 g, 40.3%). NMR analysis showed that the product was not deuterated.

Acetoxylation of 1,5-Cyclooctadiene (3): This reaction was performed using the same quantities of starting materials as in the acryloxylation of 1,5-cyclooctadiene (**3**) described above, but with AcOH as the solvent. In the ^{13}C-NMR spectrum of the crude product it was possible to detect the characteristic signals of enol acetate **5b** at δ = 116.1 (C^2), 127.6 (C^5), and 128.5 (C^6). After purification, we obtained 0.58 g (47%) of cyclooct-4-enone (**4**).

Identification of Acetic Anhydride (8) and Dienone (9) in the Reaction Mixture: In order to identify acetic anhydride in the reaction mixture by ^{13}C NMR, which appeared to be the most reliable and efficient method, it was necessary that three requirements were fulfilled: (i) the solution had to be free from water, which would otherwise have hydrolyzed the anhydride; (ii) all traces of metals had to be removed in order to be able to record the NMR spectrum, and (iii) the bulk of the acetic acid solvent had to be removed to permit detection of the acetic anhydride signals. In order to achieve a deuterium lock, perdeuterated acetic acid was employed. The reaction was carried out under the usual conditions and, after reaching completion, the mixture was diluted with pentane, filtered through Celite to remove all solid particles, and the filtrate was concentrated. The solution thus obtained was subjected to ^{13}C-NMR analysis. The spectrum featured the usual signals of enone **4**, plus those of acetic acid (δ = 175.9 and 20.8) and of acetic anhydride (**8**) (δ = 116.3 and 21.7). This solution was then neutralized with the requisite amount of solid anhydrous sodium carbonate and a small quantity of molecular sieves was added to remove the traces of water formed by the neutralization of the acetic acid. The ^{13}C-NMR spectrum of this solution no longer showed the signals of acetic acid, but those of acetic anhydride remained. The products were then purified by flash chromatography on silica. Elution with pentane gave a mixture of enone **4** and a product that was identified as 2,4-cyclooctadienone (**9**) by its ^{13}C-NMR spectrum[15] (50.3 MHz, $CDCl_3$): δ = 206.1 (q, C^1), 138 (t, C^3), 136.9 (t, C^5), 131.5 (t, C^4), 128.7 (t, C^2), 38.5 (s, C^8), 32.8 (s, C^7), 26.3 (s, C^6).

Oxidation of 1,5-Cyclooctadiene (3) in the Presence of the $Pd(OAc)_2$/Benzoquinone/MnO_2 Catalyst and H_2O_2: In a 5-mL flask, equipped with a magnetic stirrer and a condenser, were placed benzoquinone (22 mg, 0.2 mmol), $Pd(OAc)_2$ (22.4 mg, 0.1 mmol), 1,5-cyclooctadiene (**3**) (0.216 g, 10 mmol), and 30% H_2O_2 (0.25 mL, 3 mmol). The solution was stirred vigorously at room temperature for 22 h and then 10 mL of a 1:1 mixture of pentane/diethyl ether was added. The organic layer was washed first with brine and then with 1 M NaOH solution, dried with $MgSO_4$, filtered through Celite, and the filtrate was concentrated. The crude product was then analyzed by ^{1}H NMR and GC. The extent of formation of cyclooct-4-enone (**4**) was estimated to be 6% with a 94% conversion of 1,5-cyclooctadiene (**3**).

Synthesis of Cycloocta-1,5-dienyl Acetate (5b): In a 250-mL two-necked flask fitted with a Vigreux distillation column were placed cyclooct-4-enone (**4**) (1.3 g, 10.7 mmol), and a solution of 0.612 g (3.2 mmol, 0.3 equiv.) of *p*-toluenesulfonic acid in isopropenyl acetate (77.5 mL). A very slow distillation was then carried out for around 20 h. The initially colorless reaction medium became progressively more yellow and eventually turned brown. The first fraction, distilling at 55−60°C, consisted of acetone, which was followed by isopropenyl acetate (90−98°C). In order to maintain the overall volume of the reaction medium at around 20 mL, further isopropenyl acetate was constantly added throughout the process. The reaction medium was subsequently allowed to cool and then extracted with diethyl ether. The organic phase was washed several times with a cold saturated solution of sodium hydrogen carbonate until all traces of acid were removed, and was then washed twice with water and twice with brine. It was then dried with sodium sulfate and concentrated in a rotary evaporator, which removed the remainder of the isopropenyl acetate. The crude product thus obtained was then purified by flash chromatography on silica to afford 450 mg (25.3%) of pure cycloocta-1,5-dienyl acetate (**5b**) (R_f = 0.8, pentane/diethyl ether, 1:1). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.9−5.5 (m, 3 H, H^2, H^5 and H^6), 2.35−2.2 (m, 4 H), 2.15 (s, 3 H, H^{10}), 1.7−1.3 (m, 4 H). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 169.7 (q, C^9), 150.0 (q, C^1), 128.5 (t, C^6), 127.6 (t, C^5), 116.1 (t, C^2), 31.1 (s, C^3), 27.7 (p, C^{10}), 26.6 (s, C^4), 23.9 (s, C^8), 20.9 (s, C^{10}). − IR ($CHCl_3$): $\tilde{\nu}$ = 2900 (C=C), 1740 (C=O), 1650 (C=C), 1360 (C−O), 1190 (C−O). − $C_{10}H_{14}O_2$ (166.21): calcd. C 72.26, H 8.48; found C 71.97, H 8.40.

Acetoxylation of Cycloocta-1,5-dienyl Acetate (5b): In a 10-mL flask fitted with a condenser were placed $Pd(OAc)_2$ (6 mg, 0.025 mmol), benzoquinone (11 mg, 0.1 mmol), MnO_2 (52 mg, 0.6 mmol), and acetic acid (3 mL). The mixture was stirred at room temperature for 30 min and then a solution of cycloocta-1,5-dienyl acetate (**5b**) (83 mg, 0.5 mmol) in acetic acid (1 mL) was added. The resulting mixture was heated to 60°C for 48 h and the reaction was carried out as described above. Analysis of the crude product by GC and ^{1}H NMR showed the yield of cyclooct-4-enone (**4**) to be ca. 50%, with a 50% conversion.

Acryloxylation of a 1,5-Cyclooctadiene−Pd^0−*p*-Benzoquinone Complex: In an NMR tube were placed 53 mg of 1,5-cyclooctadiene−Pd^0−*p*-benzoquinone complex **A**, prepared according to literature procedures,[7][13] together with 0.4 mL of $CDCl_3$. Freshly distilled acrylic acid (1 μL) was then added and the tube was recapped and shaken. The reaction was immediately monitored by ^{1}H NMR (300 MHz) without prior temperature equilibration. − ^{1}H NMR (300 MHz): δ = 1.62 ($H^{8\beta}$), 2.14 (H^3), 2.35 ($H^{8\alpha}$), 2.42 (H^7), 2.63 ($H^{4\beta}$), 2.90 ($H^{4\alpha}$), 3.12 (H^1), 5.34 (H^2), 5.42 (H^5), 5.85 (H^6), 5.95 ($H^{11\ cis}$ acrylate), 6.15 (H^{10} acrylate), 6.5 ($H^{11\ trans}$ acrylate). The proton signals of benzoquinone, which appeared at δ =

5.75 in **A**, were now seen at δ = 6.70, a chemical shift corresponding to the protons of hydroquinone.

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