Two-step oxidative one pot functionalization of 2-benzylidene-1-tetralone in the $Pd^{II}/Cu^{II}/Na_2CO_3$—MeOH system: a novel route to 2-(α-methoxy)benzyl-1,4-naphthoquinone

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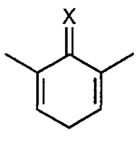
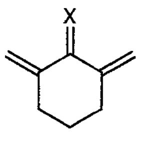
A novel two-step oxidative one pot functionalization of 2-benzylidene-1-tetralone by its reaction with Na_2PdCl_4 in the presence of $CuCl_2$ and Na_2CO_3 (in 1 : 1 : 2 : 5 molar ratio) in MeOH was discovered. The reaction yields 2-(α-methoxy)benzyl-1,4-naphthoquinone.

Key words: oxidative functionalization; one pot synthesis; 2-benzylidene-1-tetralone; 1,4-naphthoquinones; Pd^{II} derivatives in organic synthesis.

The use of semiquinoid (**1**) and isomeric isosemiquinoid (**2**) π-systems is very promising for our works on the "cascade" building of polyconjugated heteroorganic ligands and their metal complexes.[1] Previously[2] we discovered oxidative *exo*-alkoxylation of 2,6-dibenzylidenecyclohexanone (**3**) through the action of Pd^{II} salts in MeOH, which gives methoxydienone **4**.



1



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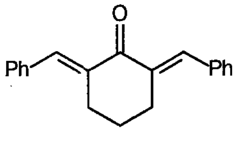

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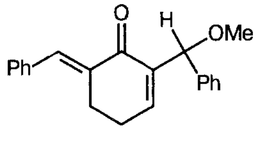

4

In the present work we found that the reaction of a benzo analog of compound **3**, 2-benzylidene-1-tetralone (**5**),[3] with Na_2PdCl_4 (in the presence of $CuCl_2$ and Na_2CO_3) in MeOH is not limited to *exo*-alkoxylation (with expected aromatization of benzosemiquinoid intermediate **6**), but is accompanied by deeper oxidation of the molecule (Scheme 1), which probably proceeds *via* intermediate organopalladium compounds of the π-allylic type (**7a**) or even of the quinolide type (**7b**). The quinone structure of the final product (**8**) was established by elemental analysis and also by comparing the spectra of compound **8** with the spectra of known *p*-quinones (see Ref. 4).

The structure of **8** was confirmed by the fact that its IR spectrum exhibits characteristic intense absorption bands of the conjugated carbonyl group and the conjugated double bond and by the mass-spectral fragmentation of the molecular ion that involves the loss of O, (CO + Me) and the formation of C_4H_2, C_6H_4, Ph, PhCH(OMe), which is typical of *p*-quinones.*

The reaction found (*cf.* other processes of the allylic oxidation of alkenes by Pd^{II} salts)[5,6] extends the scope of the transformations of isosemiquinoid ligands and may be of interest as a novel strategy for the synthesis of biologically active naphthoquinone systems.

Experimental

All of the solvents were distilled just prior to use; methanol was dehydrated with magnesium methylate according to the standard procedure.[7] Chromatographic separation was carried out using silica gel or commercial plates with silica gel from Chemapol (Czechoslovakia). IR spectra were recorded on a UR-20 spectrophotometer in Vaseline oil, UV spectra were measured on a Specord UV-VIS spectrophotometer in CH_2Cl_2, and mass spectra were obtained on an AEI MS-30 instrument (70 eV). ^1H NMR spectra were recorded on a Bruker WP-200SY instrument (200 MHz) in $CDCl_3$.

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* It is noteworthy that the mass spectrum of compound **8**, along with the normal routes of fragmentation, exhibits a contribution of unusual fragmentation with the loss of $Me^{\bullet}$. This is also a characteristic feature of other cross π,π-conjugated systems that we have prepared previously in which the CO groups and CH(OMe) fragments are arranged close to each other.

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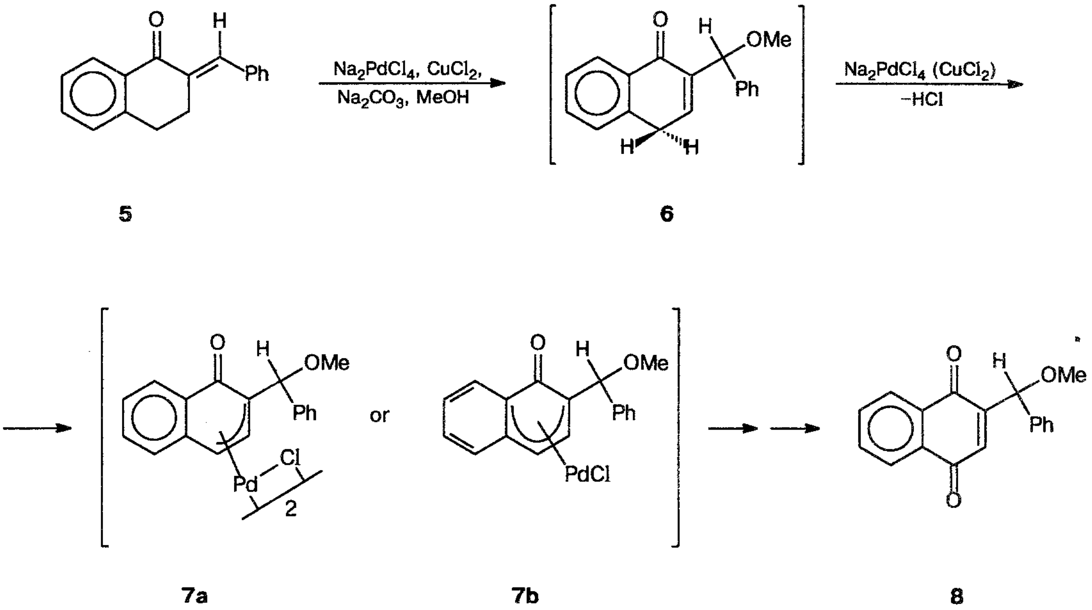
Scheme 1



2-(α-Methoxybenzyl)-1,4-naphthoquinone (8). A suspension of 0.117 g (0.5 mmol) of tetralone **5**, 0.147 g (0.5 mmol) of Na_2PdCl_4, 0.135 g (1.0 mmol) of $CuCl_2$, and 0.5 g of Na_2CO_3 in 15 mL of anhydrous MeOH was stirred with a magnetic stirrer for 40 h at 20 °C and filtered. The precipitate was washed with $CHCl_3$ (5×10 mL) on the filter, and the combined filtrates were concentrated to dryness. The residue was dissolved in 30 mL of MeOH and filtered through a 3 cm layer of 40/100 μ silica gel to remove inorganic impurities. The adsorbent was washed with EtOAc and the combined eluates were concentrated. The residue was chromatographed on a column (d = 1.6 cm, l = 20 cm) packed with Silpearl 029 silica gel (using CH_2Cl_2—hexane, 1 : 1, as the eluent), and the fractions with R_f 0.54 and 0.37 (Silufol UV-254 plates, CH_2Cl_2) were collected. The first fraction contained unchanged tetralone **5**. Evaporation of the solvent from the second fraction yielded 0.030 g (22 %) of product **8** as a yellow crystalline material, m.p. 93—97 °C. Found (%): C, 77.95 and 77.83; H, 5.09 and 4.85. $C_{18}H_{14}O_3$. Calculated (%): C, 77.70; H, 5.04. IR, ν/cm^{-1}: 1600 (C=C); 1660 (C=O); 1630 (Fermi resonance). UV, λ_{max}/nm (log ε): 247 (4.74), 253 (4.75), 333 (3.85). ^{1}H NMR, δ: 3.38 (s, 3 H, OCH_3); 5.50 (d, 1 H, CH(α), $J_{H(\alpha)-H(3)}$ = 1.5 Hz); 7.21 (d, 1 H, H(3), $J_{H(3)-H(\alpha)}$ = 1.5 Hz); 7.3—8.1 (m, 9 H, C_6H_4 and C_6H_5). MS (EI), m/z (I_{rel} (%)): 278 [M$^+$] (13), 263 [M−Me] (36), 261 [M−OH] (75), 246 [M−MeOH] (95), 157 [M−PhCHOMe] (22), 121 [PhCHOMe] (93), 105 [PhCO] (38), 91 [C_7H_7] (29), 50 [C_4H_2] (20).

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