Autoxidative Decarbonylation of a Stable Enol from Diels–Alder Addition of 2-Methoxy-5-methylbenzoquinone to Sorbic Acid Esters

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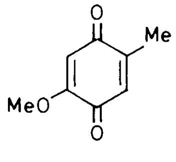
The reaction of 2-methoxy-5-methylbenzoquinone (**1**) and methyl sorbate (**2a**) gives mainly the enol, the Diels–Alder adduct (**5a**), which undergoes oxidative ring-cleavage *via* the hydroperoxide (**7a**) to give the β-ketoester (**8a**) in a good yield.

The Diels–Alder reactions of *p*-benzoquinones have been widely utilized in the synthesis of various natural products[1] as well as strained polycyclic compounds.[2] These reactions generally proceed with high stereo- and regio-selectivity to give products explained in terms of frontier molecular orbital (FMO) theory.[3] However, the Diels–Alder reactions of substituted benzoquinones such as 2-methoxy-5-methylbenzoquinone (**1**) sometimes display very poor selectivity and the results are not predictable.[4—6]

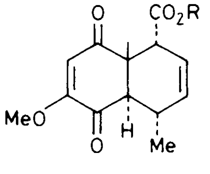
In a study on the cycloaddition reactions of benzoquinone, we have found that the Diels–Alder reactions of (**1**) with the sorbic acid esters (**2**) give enol products which undergo facile oxidative rearrangement to the β-ketoester compound. Bohlmann and co-workers[4] reported that the reaction of (**1**) with methyl sorbate (**2a**) at 110 °C gave the *trans*-adduct (**3a**) (51%) together with several minor products including its regioisomers and dehydrogenation products, but none of the *cis*-adduct (**4a**), a plausible primary product. We have re-examined the reaction under different conditions. When (**1**) reacted with an excess (8 equiv.) of (**2a**) without solvent at 100 °C for 67 h under Ar (54% conversion), a new adduct (**5a**)† was obtained as the major product (67%) together with (**3a**) (5%) and two other known minor products.[4] The enol structure of (**5a**), m.p. 160—161 °C, was apparent from its spectroscopic data [i.r., ν_{max} 3310, 1740, 1670 cm^{-1}; ^{1}H n.m.r., δ ($CDCl_3$) 1.28 (s, 3H), 1.34 (d, *J* 7.0 Hz, 3H), 3.2—3.4 (m, 1H), 3.6—3.7 (m, 1H), 3.60 (s, 3H), 3.88 (s, 3H), 5.40 (s, 1H), 5.41 (s, 1H, D_2O-exchangeable), 5.48 (m, 2H); ^{13}C n.m.r., δ 203.5 (s, C-4), 172.5 (s, CO_2R), 164.7 (s, C-2), 137.2 (s, C-1), 129.0 p.p.m. (s, C-9); mass spectrum, *m/z* 278 (M^+)] and from its ready conversion (Ac_2O–pyridine) into the acetate (**6**)† (80%), m.p. 124—125 °C. While (**5a**) could be considered derived from *cis*-(**4a**), formation of (**4a**) was not observed even under milder conditions. On the other hand, heating (**5a**) at 120 °C under Ar gave *trans*-(**3a**) as well as dehydrogenation products.[4]

While (**5a**) was stable in the solid state, gradual aerial oxidation occurred in solution ($CHCl_3$ and/or ethyl acetate)

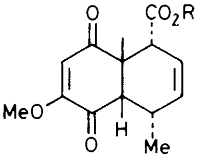


(**1**)

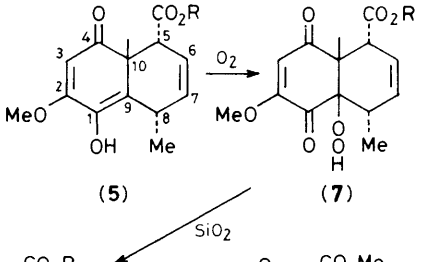
(**2**)



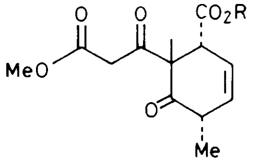
(**3**)



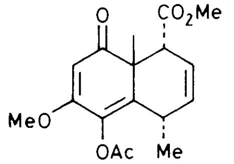
(**4**)



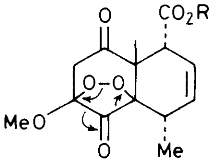
(**5**) (**7**)



(**8**)

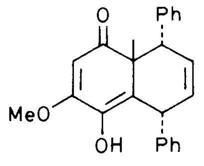


(**6**)

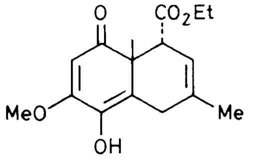


(**9**)

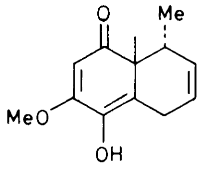
a; R = Me
b; R = Et



(10)



(11)



(12)

and the crystalline hydroperoxide (**7a**)† was obtained in 70% yield after 20 h at room temperature in an open beaker [m.p. 117—118 °C; i.r., ν_{max} 3440 cm^{-1}; ^{1}H n.m.r., δ 9.89 (s, 1H, D_2O-exchangeable); ^{13}C n.m.r., δ 91.6 (s, C-9); mass spectrum, *m/z* 310 (M^+)]. Interestingly, this transformation was retarded by addition of D_2O, which suggested an ene-type reaction between the enol and oxygen. Percolation of a chloroform solution of (**7a**) through a silica gel column resulted in a spontaneous evolution of gas to give the β-ketoester (**8a**)† (90%) [m.p. 120—121 °C; i.r. ν_{max} 1750br., 1720 cm^{-1}; ^{1}H n.m.r., δ 1.27 (d, *J* 7.0 Hz, 3H), 1.57 (s, 3H), 3.08 (q, *J* 7.0 Hz, 1H), 3.4—3.5 (m, 1H), 3.66 (s, 3H), 3.72 (s, 3H), 3.85 (s, 2H, exchanged by D_2O–NaOD), 5.8—5.9 (m, 2H); ^{13}C n.m.r., δ 207.8, 202.5, 172.6, 167.8 p.p.m. (each s); mass spectrum *m/z* 282 (M^+)]. The formation of (**8a**) can be explained by decarbonylation[7] of the endoperoxide (**9a**) initially formed by intramolecular addition of the hydroperoxy group to the C-2–C-3 double bond in (**7a**). The reaction of (**1**) with ethyl sorbate (**2b**) also gave the enol adduct (**5b**)† (54%), m.p. 151—152 °C, which was similarly converted into the β-ketoester (**8b**)†, m.p. 76—77 °C, *via* (**7b**) in 76% overall yield.

The isolation of enol compounds with no special stabilizing functionality (simple enols)[8] like (**5**) is noteworthy. The enol products, (**10**) and (**11**),† were also isolated from the reaction of (**1**) with 1,4-diphenylbuta-1,3-diene and ethyl 4-methylpenta-2,4-dienoate, respectively. Recently, Tou and Reusch[9] have also reported the isolation of (**12**) from the Lewis-acid catalysed reaction of (**1**) with piperylene. The presence of the methoxy group at C-2 in the cycloadduct of (**1**) seems to be an important factor in the formation of the enol tautomer since similar reactions of 2,5-dimethylbenzoquinone gave no enol products.

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† All new compounds gave satisfactory analytical and spectral data.