The Reaction of 2-Acetyl-1,4-benzoquinone with Alcohols. A Convenient Synthesis of 2-Acetyl-3-alkoxy-1,4-benzoquinones

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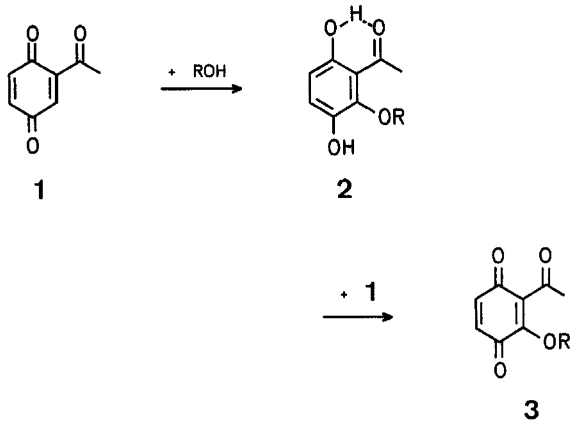
The reaction of 2-acetyl-1,4-benzoquinone with various nucleophiles (furans, thiophenes, vinyl ethers, acetoacetic ester) has been the subject of several publications[1,2]. However, the reaction with alcohols has never been reported.

Recent work in our laboratories has shown that 2-acetyl-1,4-benzoquinone (**1**) reacts with alcohols under unusually mild conditions and, depending on the proportion of the reactants, the 2-acetyl-3-alkoxyhydroquinone (**2**) or the 2-acetyl-3-alkoxy-1,4-benzoquinone (**3**) can be isolated:



The U.V. spectrum of **1** determined by us in cyclohexane [$\lambda_{max}^{cyclohexane}$: 246 m$\mu$ (log $\varepsilon = 4.07$)] is not the same as that previously reported[1] using ethanol as solvent [$\lambda_{max}^{ethanol}$: 214 (4.03), 264 (3.81), 370 (3.42)]. This is evidence for a rapid reaction of **1** with ethanol.

The presence of the acetyl group in the quinone **1** enhances greatly the reactivity of the 3-position and nucleophilic addition takes place only at this position, under very mild conditions. The process involves a conjugate addition of the weakly nucleophile ROH to the C=C—C=O system of the quinone and does not require any catalysis.

The reaction of 2-acetyl-1,4-benzoquinone (**1**) with an excess of the alcohol ROH (the alcohol serving as the solvent) at room temperatures gives only low yields of the corresponding 2-acetyl-3-alkoxyhydroquinone (**2**) which is accompanied by oxidation products of the alcohol, some quinone **3**, and 2-acetylhydroquinone. The physical constants, analyses, and spectral data of the 2-acetyl-3-alkoxyhydroquinones (**2**) obtained are summarized in Table 1.

When the reaction is carried out in an inert solvent employing equimolar quantities of quinone (**1**) and alcohol, high yields of 2-acetyl-3-alkoxy-1,4-benzoquinones (**3**) are obtained. Compounds **3** are formed by oxidation of the primary reaction products **2** by quinone **1**. Aliphatic, cycloaliphatic, and araliphatic primary and secondary alcohols can be used in the reaction. *t*-Butanol does not react, probably due to steric factors. The reaction provides a simple method for the synthesis of quinones of the type **3**, which are not easily available by other methods. Yields, analyses, physical constants, and spectral data of compounds **3** thus prepared are listed in Table 2. The hydroquinones **2** are readily obtained by reduction of quinones **3** using conventional methods.

Similar additions of alcohols to other *p*-benzoquinones bearing electron-withdrawing substituents have been observed; these reactions will be reported in a forthcoming paper.

2-Acetyl-3-alkoxy-1,4-benzoquinones (3) from 2-Acetyl-1,4-benzoquinone (1) and Alcohols; General Procedure:

To a solution of 2-acetyl-1,4-benzoquinone (**1**) in dry benzene was added, at room temperature, an equimolar amount of the alcohol. The resultant solution was allowed to stand for 2 days with

Table 1. 2-Acetyl-3-alkoxyhydroquinones (**2**)

R	m.p.	Analysis	I.R.[a]		N.M.R.[b]					
			O—H	C=O	(s) OH		(d) arom.		(s) 3H Ac	others
					C_1	C_4	C_5	C_6		
$-CH_3$	90°[c]		3280	1630	−2.12	4.55	2.82	3.25	7.24	6.12 (s, 3H)
$-C_2H_5$	102–103.5°	calc. C 61.2 H 6.1 found 61.5 6.1	3300	1630	−1.92	4.45	2.85	3.34	7.26	6.00 (q, 2H) 8.56 (t, 3H)
i-C_3H_7	90–92°	calc. C 62.9 H 6.7 found 63.1 6.8	3290	1640	−1.52	4.44	2.78	3.22	7.18	5.62 (m, 1H) 8.57 (d, 6H)
n-C_4H_9	62.5–63.5°	calc. C 64.3 H 7.1 found 64.6 7.4	3300	1645	−1.66[d]	4.66	3.03	3.48	7.36	6.16 (t, 2H) 8–9.1 (m, 7H)
$-CH_2-CH=CH_2$	68–69°	calc. C 63.5 H 5.8 found 63.2 5.8	3290	1630	−1.87	4.67	2.93	3.33	7.28	5.58 (m, 2H) 3.5–4.8 (m, 3H)
c-C_6H_{11}	75–76.5°	calc. C 67.2 H 7.3 found 67.5 7.5	3330	1630	−1.32	4.73	2.95	3.36	7.30	~6.2 (m, 1H) 7.8–9.0 (m, 10H)
$-CH_2-C_6H_5$	87.5–89°	calc. C 69.8 H 5.4 found 70.0 5.7	3340	1630	−1.86	4.90	2.60	2.89	7.28	2.60 (s, 5H) 5.06 (s, 2H)

[a] KBr; $\tilde{\nu}$ [cm^{-1}].

[b] τ values in $CDCl_3$; TMS as internal standard.

[c] Ref.[3], m.p. 90°.

[d] In CCl_4.

Table 2. 2-Acetyl-3-alkoxy-1,4-benzoquinones (**3**)

R	Yield[c] %	b.p./mm	Analysis	I.R.[a]		N.M.R.[b]		
				C=O	C=C	(s) 2 H C_5—C_6	(s) 3 H Ac	others
—CH_3	95	104–105°/0.4	calc. C 60.0 H 4.4 found 60.3 4.6	1715 1680 1650	1590	3.27	7.56	5.94 (s, 3 H)
—C_2H_5	100	108–109°/0.4	calc. C 61.9 H 5.2 found 61.7 4.9	1705 1670 1640	1585	3.32	7.56	5.65 (q, 2 H) 8.65 (t, 3 H)
i-C_3H_7	90	87–89°/0.2	calc. C 63.5 H 5.8 found 63.6 6.0	1712 1675 1645	1585	3.31	7.56	4.87 (m, 1 H) 8.68 (d, 6 H)
n-C_4H_9	93	120–121°/0.9	calc. C 64.9 H 6.3 found 64.9 6.2	1710 1675 1645	1580	3.30	7.55	5.70 (t, 2 H) 8–9.1 (m, 7 H)
—CH_2—CH=CH_2	74	—[d]	—[e]	1705 1670 1640	1585	3.28	7.55	3.7–4.9 (m, 3 H) 5.15 (m, 2 H)
c-C_6H_{11}	82	135–136°/1	calc. C 67.7 H 6.5 found 67.9 6.3	1712 1675 1645	1585	3.31	7.58	5.17 (m, 1 H) 7.7–9.0 (m, 10 H)
—CH_2—C_6H_5	84	—[d]	—[e]	1710 1675 1650	1585	3.30	7.68	2.63 (s, 5 H) 4.60 (s, 2 H)

[a] Liquid film, $\bar{\nu}$ [cm^{-1}].

[b] τ values in $CDCl_3$; TMS as internal standard.

[c] The yields given refer to the reaction as a whole, i.e., yields are based on 50% of the quantity of quinone **1** subjected to the reaction.

[d] The product decomposes under the distillation conditions.

[e] Identified by I.R. and N.M.R. spectra.

exclusion of light. The solvent and excess alcohol were then distilled off. The residue was extracted in the cold with carbon tetrachloride and the remaining insoluble 2-acetylhydroquinone removed by filtration. On evaporation of the carbon tetrachloride extract, the 2-acetyl-3-alkoxy-1,4-benzoquinone (**3**) was obtained as a red oil. The product was essentially pure. Analytical samples were obtained by distillation in vacuo.

The quinones are moderately stable but storage in a refrigerator is recommended in order to avoid slow decomposition.

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[1] C. H. Eugster, P. Bosshard, Helv. Chim. Acta **46**, 815 (1963).

[2] C. H. Eugster, P. Kuser, Chimia **18**, 358 (1964).
P. Bosshard, S. Fumagalli, R. Good, W. Trueb, W. v. Philipsborn, C. H. Eugster, Helv. Chim. Acta **47**, 769 (1964).
N. Baumann, S. Fumagalli, G. Weisgerber, C. H. Eugster, Helv. Chim. Acta **49**, 1794 (1966).

[3] K. Wallenfels, Chem. Ber. **75**, 785 (1942).