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The Formation of Acetylcatechol in the Photochemical Reaction of *o*-Benzoquinones with Acetaldehyde

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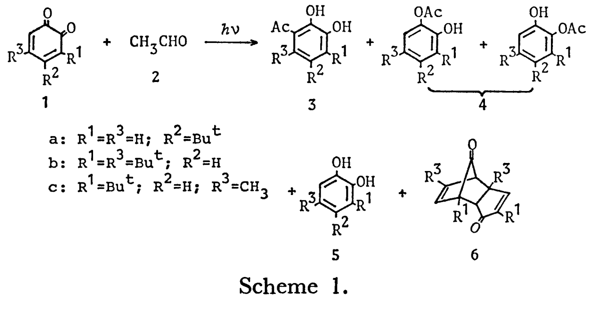
Synopsis. The irradiation of several alkyl-substituted *o*-benzoquinones in the presence of acetaldehyde gave the corresponding acetylcatechol and catechol monoacetates *via* the attack of the acetyl radical on the ground-state quinone molecule. In the reaction of 3,5-di-*t*-butyl- and 3-*t*-butyl-5-methyl-*o*-benzoquinones, the dimer of alkyl-substituted cyclopentadienone, generated by the photodecarbonylation of the quinones, was also obtained.

There have been reported only a few examples of photochemical reactions between *o*-benzoquinone and aldehyde.[1] For example, tetrachloro- and tetrabromo-*o*-benzoquinones usually give the tetrahalocatechol monoesters in a reaction with acetaldehyde and benzaldehyde.[1] In these quinones, the reactive quinonoid bonds are completely replaced with halogen atoms. We ourselves reported recently that 3-acetyl-1,2-naphthalenediol was formed, together with a mixture of 1,2-naphthalenediol monoacetates, in the photochemical reaction of 1,2-naphthoquinone with acetaldehyde.[2] It was, therefore, of interest to examine the possibility of introducing an acetyl group into the quinonoid nucleus of *o*-benzoquinone. In this paper we wish to report the product analyses and reaction courses of the photochemical reactions of mono- and dialkyl-substituted *o*-benzoquinones with acetaldehyde.

The irradiation of a benzene solution of 4-*t*-butyl-*o*-benzoquinone (**1a**) in the presence of a large excess of acetaldehyde (**2**) gave acetylcatechol (**3a**) (20%) and an isomeric mixture of catechol monoacetates (**4a**) (20%). The structures of the products were confirmed by their spectral data and elemental analyses.

The photo-induced reaction of 3,5-di-*t*-butyl-*o*-benzoquinone (**1b**) with **2** produced **3b**, **4b**, **5b**, and the dimer (**6b**) of 2,4-di-*t*-butylcyclopentadienone (CPD) in 6, 36, 22, and 4.5% yields respectively. 3-*t*-Butyl-5-methyl-o-benzoquinone (**1c**) similarly reacted with **2** to give **3c** (12%), **4c** (14%), and **6c** (1%), but no **5c** could be isolated (Scheme 1).

Recently, CPD was obtained from the UV irradiation of **1b**, and it dimerized at room temperature to give **6b** in the mode of Diels-Alder reaction.[3] Actually, two dimers, **6b** and **6c**, were obtained, in yields of 50 and 43% respectively, from the photolysis of a benzene solution of **1b** and **1c** in the absence of **2**; carbon monoxide was also evolved.



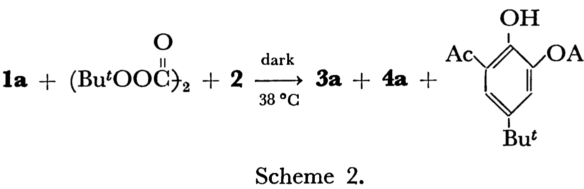
Scheme 1.

Thus, the irradiation of mono- and dialkyl-substituted *o*-benzoquinones in **2** gives acetylcatechols, together with catechol monoacetates, although a little photodecarbonylation occurs when **1b** and **1c** are irradiated in the aldehyde.

As for the mechanism of the formation of acetylcatechol and catechol monoacetates, two possibilities have been considered. One is an "in-cage" mechanism, *i.e.*, a process involving the combination of the radical pair consisting of *o*-benzosemiquinone and acetyl radicals in the solvent cage formed by the abstraction of formyl hydrogen from **2** by the excited quinone. The photo-CIDNP technique provides invaluable information for investigating such a radical-pair process.[2] Since, however, no ^{1}H-CIDNP signals could be observed in the reaction of **1a** with **2**, such an "in-cage" mechanism can be excluded.

An alternative mechanism is an "out-of-cage" one, *i.e.*, a process involving the addition of the free acetyl radical which escaped from the solvent cage to ground-state quinone.[2] In order to clarify the possibility, the addition reaction of the free acetyl radical to **1a** in the ground state was undertaken. The treatment of a benzene solution of **1a** and **2** with di-*t*-butyl diperoxyoxalate (DTBP)[4] in the dark allowed us to generate the necessary reacting conditions. When the decomposition of DTBP was carried out at 38 °C in a benzene solution of **1a** and **2**, **3a** and **4a**, which were the same products as those obtained from the photochemical reaction, were isolated in yields of 26 and 7% respectively; a diacetylated product (**7**) was also isolated in a yield of 6% (Scheme 2).

A benzene solution of **3a** and **2** was treated with DTBP to give **7** in a 25% yield. A similar treatment of **4a**, however, led to an almost quantitative recovery


$$\mathbf{1a} + (\mathrm{Bu}^t\mathrm{OO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}})_2 + \mathbf{2} \xrightarrow[38\,^\circ\mathrm{C}]{\text{dark}} \mathbf{3a} + \mathbf{4a} +$$

(**7**)

Scheme 2.

$$\mathrm{Q} \xrightarrow{h\nu} \mathrm{Q^S} \xrightarrow{\text{i.s.c.}} \mathrm{Q^T}$$

$$\mathrm{Q^T} + \mathrm{CH_3CHO} \longrightarrow \overline{\cdot\mathrm{QH},\ \mathrm{CH_3\dot{C}O}}^{\,\mathrm{T}} \xrightarrow{\text{diffusion}}$$

$$\cdot\mathrm{QH} + \mathrm{CH_3\dot{C}O}$$

$$\mathrm{Q} + \mathrm{CH_3\dot{C}O} \xrightarrow{\cdot\mathrm{QH}} \mathbf{3a} + \mathbf{4a}$$

Q: 4-*t*-Butyl-*o*-benzoquinone
·QH: 4-*t*-Butyl-*o*-benzosemiquinone radical

Scheme 3.

TABLE 1. SOME PHYSICAL DATA OF REDUCTIVE ACETYLATION PRODUCTS

Compound	Mp θ_m/°C[a]	IR(KBr) $\tilde{\nu}$/cm^{-1}		Found(%)		Calcd(%)	
		OH	C=O	C	H	C	H
3a	82—83[b]	3420	1620	69.28	7.77	69.21	7.74
4a	Oil	3400	1760[d]	69.16	7.69	69.21	7.74
3b	169—170[b]	3400	1680	72.49	9.13	72.69	9.15
4b	118—119[c]	3400	1750	72.55	9.18	72.69	9.15
3c	72—73[b]	3470	1620	70.22	8.24	70.24	8.16
4c	Oil	3430	1735[e]	70.16	8.17	70.24	8.16

a) Melting points are uncorrected. b) Recrystallized from light petroleum. c) Recrystallized from benzene-light petroleum. d) Solvent: $CHCl_3$. e) Solvent: CCl_4.

TABLE 2. ^{1}H-NMR DATA OF REDUCTIVE ACETYLATION PRODUCTS

Compound	δ(CCl_4)
3a	1.30(s, *t*-Bu), 2.56(s, $COCH_3$), 5.46(s, OH), 7.04(d, *J*=3.0 Hz, aromatic proton), 7.08(d, *J*=3.0 Hz, aromatic proton), 12.16(s, OH)
4a	1.20(s, *t*-Bu), 1.22(s, *t*-Bu), 2.07(s, $OCOCH_3$), 2.10(s, $OCOCH_3$), 6.60—6.96(m, OH's and aromatic protons)
3b	1.31(s, *t*-Bu), 1.39(s, *t*-Bu), 2.55(s, $COCH_3$), 5.57(s, OH), 6.05(s, OH), 6.88(s, aromatic proton)[a]
4b	1.24(s, *t*-Bu), 1.28(s, *t*-Bu), 1.32(s, *t*-Bu), 1.38(s, *t*-Bu), 2.27(s, $OCOCH_3$), 2.29(s, $OCOCH_3$), 5.24(s, OH), 5.28(s, OH), 6.68(s, aromatic protons)
3c	1.36(s, *t*-Bu), 2.45(s, CH_3), 2.55(s, $COCH_3$), 5.93(s, OH), 6.46(s, aromatic proton), 13.16(s, OH)
4c	1.27(s, *t*-Bu), 1.36(s, *t*-Bu), 2.07(s, CH_3), 2.13(s, CH_3), 2.18(s, $OCOCH_3$), 2.24(s, $OCOCH_3$), 5.55(s, OH), 6.17—6.74(m, OH's and aromatic protons)

a) Solvent: chloroform-*d*.

of the starting material. These results suggest that **7** may arise *via* **3a**. In addition, the photo-induced Fries rearrangement of **4a** to **3a** is unlikely under the irradiation conditions in this work, since **4a** does not absorb in the visible region. These results strongly supported the "out-of-cage" process for the mechanism of the present photo-induced reductive acetylation (Scheme 3).

Experimental

The IR, ^{1}H-NMR, and ^{13}C-NMR spectra were recorded on a Hitachi 215 spectrometer, a JEOL MH-100 spectrometer (internal TMS standard), and JEOL FX-100 FT NMR spectrometer respectively. Microanalysis was carried out on a Yanaco MT-2 CHN corder. The yields are based on the quinone used.

Materials. 4-*t*-Butyl- and 3,5-di-*t*-butyl-o-benzoquinones(**1a** and **1b**) were prepared by the oxidation of the corresponding catechols with silver oxide; **1a**: mp 66—68 °C (lit,[5] 68 °C). **1b**: mp 113—114 °C(lit,[3] 114—115 °C). 3-*t*-Butyl-5-methyl-*o*-benzoquinone(**1c**) was prepared by the oxidation of 2-*t*-butyl-4-methylphenol with Fremy's salt; **1c**, IR(KBr): $\nu_{C=O}$ 1660 cm^{-1}, mp 68—70 °C. DTBP was prepared according to the method described in the literature.[4]

General Procedures. A benzene solution (60 ml) of *o*-benzoquinone (2 mmol) and an excess of **2**(10 ml) was irradiated (>400 nm; Toshiba glass filter: VY-42) with a light from a 300W high-pressure Hg arc lamp through a 5 cm-thick layer of cold water (5 °C). When the *o*-benzoquinone had mostly disappeared, the solvent was removed *in vacuo*; then, the resulting oil was chromatographed by means of preparative TLC and eluted with benzene. The products thus obtained were purified by recrystallization from appropriate solvents or by TLC. The melting points, spectroscopic properties, and analytical data of the reductive acetylation products are given in Tables 1 and 2.

*Photolyses of **1b** and **1c**.* A pyrex test tube was charged with **1b** (1 mmol) or **1c** (1 mmol) and benzene (20 ml). The solution was then irradiated for 2 days. The volumes of carbon monoxide evolved during the photolyses of **1b** and **1c** were 11.7 and 10.5 ml respectively. After the removal of the benzene under reduced pressure, the resulting oil was chromatographed by means of TLC to give **6b**(50%) and **6c**(43%) respectively. **6b**: needles from ethanol; mp 153—154 °C(lit,[3] 152.5—153 °C). **6c**: needles from ethanol; mp 110—111 °C. IR(KBr) 1780(C=O) and 1696(C=O) cm^{-1}. ^{1}H-NMR(CCl_4): δ=1.10(s, 9H), 1.34(s, 3H), 1.72 (d, *J*=2.0 Hz, 3H), 2.28(s, 1H), 2.43(s, 1H), 5.58(q, *J*=2.0 Hz, 1H), and 6.66(s, 1H). ^{13}C-NMR($CDCl_3$): δ=204.9 (s), 200.6(s), 158.5(s), 155.1(d), 139.8(s), 125.8(d), 67.3(s), 61.1(d), 53.9(d), 44.8(s), 32.0(s), 31.0(s), 28.3(q), 27.1(q), 21.5(q), and 18.3(q). Found: C, 79.79; H, 9.44%. Calcd for $C_{20}H_{28}O_2$: C, 79.96; H, 9.39%. The dimers, **6b** and **6c**, were also obtained, in yields of 4.5 and 1% respectively, from the photochemical reactions of **1b** and **1c** with **2** (see Scheme 1).

Reaction Involving DTBP. *(a)*: A benzene solution of **1a** (1.5 mmol), **2** (4 ml), and DTBP (1.5 ml) was kept in the dark at 38 °C for 7 h. The resulting yellow solution was concentrated *in vacuo*, and then the residual oil was chromatographed on TLC to give **3a**(26%), **4a**(7%), and **7**(6%). **7**: pale yellow oil. IR(CCl_4): 3530(OH), 1775 (ester C=O), and 1645(C=O) cm^{-1}. ^{1}H-NMR(CCl_4): δ=1.33(s, 9H), 2.25(s, 3H), 2.60(s, 3H), 7.19(d, *J*=2.0 Hz, 1H), 7.50(d, *J*=2.0 Hz, 1H), and 12.6(s, 1H). Found: C, 67.00: H, 7.38%. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25%.

(b): A benzene solution of **3a** (0.073 mmol), DTBP (0.074 mmol), and **2**(1 ml) was kept in the dark at 38 °C for 1 h. The subsequent separation of the products by TLC gave **7**(25%) and recovered **3a**.

(c): A benzene solution(10 ml) of **4a**(0.25 mmol), DTBP (0.25 mmol), and **2**(12 mmol) was kept in the dark at 38 °C for 3 h; **4a** was recovered almost quantitatively.

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