

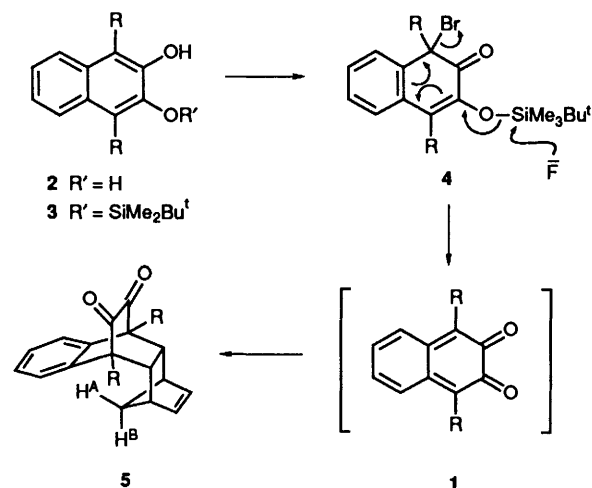
## Generation of 2,3-Naphthoquinones under Non-oxidative Conditions

David W. Jones\* and Firstborn Matthew Nongrum  
School of Chemistry, The University of Leeds, Leeds LS2 9JT, UK

The 2,3-naphthoquinones **1** (R = Ph, *o*-tolyl, CPh, Cl and Pr<sup>n</sup>) can be generated by desilylation-debromination induced by fluoride ion (**4**; arrows) and trapped as the adducts **5** with norbornadiene.

As deduced from the formation of the appropriate adducts with olefins and dienes, 2,3-naphthoquinone **1** (R = H) and its 1,4-diphenyl derivative **1** (R = Ph) are generated by oxidation of the corresponding naphthalene-2,3-diols.<sup>1,2</sup> However the adducts could have been formed by trapping radicals or other intermediates formed during the oxidation of the naphthalenediols rather than from the 2,3-naphthoquinones themselves.<sup>2</sup> We describe here a non-oxidative generation of **1** (R = Ph) by a process which, unlike the oxidative process, can be applied to several other 1,4-disubstituted 2,3-naphthoquinones.

The route adopted is outlined in Scheme 1 and was first

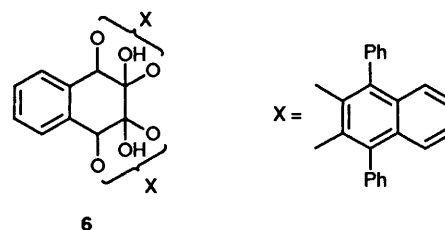


Scheme 1.

developed for **1** (R = Ph). Monosilylation of the diol **2** (R = Ph) was achieved in 89% yield by reaction with *t*-butyldimethylsilyl chloride (TBDMSC) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in CH<sub>2</sub>Cl<sub>2</sub> (20 °C, 3 h). The product was brominated with *N*-bromosuccinimide (CH<sub>2</sub>Cl<sub>2</sub>, 0–5 °C, 1 h) to give **4** (R = Ph), m.p. 115–117 °C;  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1675, which exhibited non-equivalence of the methyl groups on the silicon ( $\delta_{\text{H}}$  0.01 and 0.06). In the key step, **4** (R = Ph) eliminated cleanly (**4**; arrows) under the influence of tetra-*n*-butylammonium fluoride (TBAF) in CH<sub>2</sub>Cl<sub>2</sub>-THF at –50 °C to give a deep green colour. A similar green colour attends the generation of **1** (R = Ph) by lead tetraacetate oxidation of **2** (R = Ph). When formed from **4** (R = Ph) in THF, the visible spectrum of **1** (R = Ph) was readily recorded ( $\lambda_{\max}$  670 nm) and the green colour was shown to fade over 1 h at –50 °C. Isolation then gave the

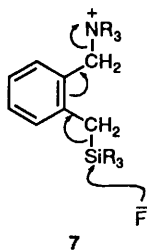
Table 1.

Adduct <b>5</b>	Yield (%) 3 → 4 → 5	<sup>1</sup> H NMR data		
		$\delta_{\text{A}}$	$\delta_{\text{B}}$	$J_{\text{AB}}/\text{Hz}$
R = Ph	64.3	–0.30	0.65	9.5
R = <i>o</i> -tolyl	43	–1.0	0.58	10.0
R = CPh	43	–0.91	0.56	10.2
R = Cl	44	0.14	0.84	10.2
R = Pr <sup>n</sup>	20	0.07	0.73	9.5



trimerides **6** which had been previously obtained by oxidation of **2** (R = Ph).<sup>2</sup> Formation of the trimerides presumably involves initial hydrogen abstraction by **1** (R = Ph) from the solvent.<sup>2</sup> Desilylation-debromination of **4** (R = Ph) in the presence of norbornadiene at –50 °C gave the adduct **5** (R = Ph) in 69.1% yield. The pronounced shielding of the methylene hydrogens (H<sup>A</sup> and H<sup>B</sup>) in the adducts **5** (Table 1) is only consistent with *endo*-selective Diels–Alder additions to the *exo* face of a norbornadiene double bond.

Whilst the oxidative route is also effective for the generation and trapping of **1** (R = *o*-tolyl) it fails for the other adducts shown in Table 1. On the other hand the non-oxidative route proceeds in the moderate (but unoptimised) yields given in Table 1 for the two stages 3 → 4 → 5. The silyl group is important in this procedure. Although an acetyl group allows formation of a bromo-compound related to **4** (R = Ph), subsequent treatment with sodium methoxide in the presence of cyclopentadiene failed to give the known<sup>2</sup> quinone-cyclopentadiene adducts. Similarly OAc cannot replace Br as leaving group in **4** (R = Ph). Our procedure is related to the Saegusa route to *o*-quinodimethanes<sup>3</sup> which is summarised in structure **7**. Our results therefore suggest that enol silyl ethers can replace the *C*-silylated group and that Br can replace the NR<sub>3</sub> leaving group in this process. This reaction should be a general one.



### Experimental

*Silylation of 1,4-Dibenzoylnaphthalene-2,3-diol.*—The title compound (100 mg), TBDMSC (82 mg), dichloromethane (4 cm<sup>3</sup>) and DBU (0.038 cm<sup>3</sup>) were stirred under argon at 20 °C (18 h). The product was isolated in ether in the usual way including washing with 0.1 mol dm<sup>-3</sup> hydrochloric acid and saturated aqueous sodium hydrogen carbonate. Short column chromatography<sup>4</sup> in benzene gave the monosilylated title compound **3** (R = C<sub>6</sub>H<sub>5</sub>) (114 mg), m.p. 179–180 °C (from methanol) (Found: C, 74.9; H, 6.25. C<sub>30</sub>H<sub>30</sub>O<sub>4</sub>Si requires C, 74.7; H, 6.2%);  $\nu_{\max}/\text{cm}^{-1}$  3546 and 1669;  $\delta_{\text{H}}(90 \text{ MHz})$  0.17 (6 H, s, 2 × Me), 7.70 (9 H, s), 7.0–8.0 (14 H, m) and 10.6 (1 H, exch. D<sub>2</sub>O).

*Trapping 1,4-Dibenzoyl-2,3-naphthoquinone with Norborna-*

*diene.*—The foregoing silyl ether (100 mg) in dry dichloromethane (2 cm<sup>3</sup>) was stirred at 0–5 °C and *N*-bromosuccinimide (37 mg) added. After it had been stirred at 0–5 °C under argon (3 h) the reaction mixture was cooled to –78 °C and freshly distilled norbornadiene (2 cm<sup>3</sup>) was added *via* a syringe, followed by TBAF in THF (0.5 cm<sup>3</sup> of 1 mol dm<sup>-3</sup> solution). The mixture was stirred at –78 °C (1 h) and then left to warm to room temperature over 2 h. The product was poured into water and isolated in ether in the usual way. The resulting oil crystallised from CH<sub>2</sub>Cl<sub>2</sub>–EtOH (40 mg, 43%), m.p. 250–254 °C (Found: C, 81.3; H, 4.8. C<sub>31</sub>H<sub>22</sub>O<sub>4</sub> requires C, 81.2; H, 4.8%);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1739, 1720 and 1679.

### References

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Paper 0/03758C

Received 15th August 1990

Accepted 24th September 1990