# Novel Nucleophilc Additions to 2,3-Dimethyl-1,4-naphthoquinone

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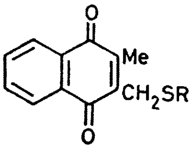
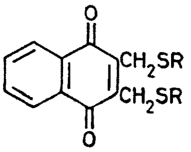
*Summary* 2,3-Dimethyl-1,4-naphthoquinone reacts with sodium benzothiazole-2-thiolate in benzene–methanol by adding the thiolate to a side-chain and methanol to the quinone ring to give the product (**4**).



(1)



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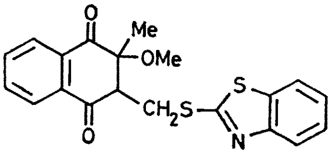

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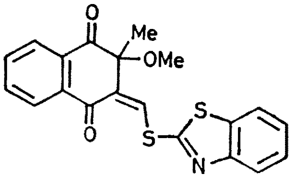

(4)

We have shown[1] that methylnaphthoquinones will react on the side-chain with an excess of sodium alkanethiolate to form alkylthiomethyl derivatives, *e.g.* (**1**) and (**2**) are obtained from 2,3-dimethyl-1,4-naphthoquinone. Arenethiolates react in the same way, but less readily. We now report an unexpected reaction with a heteroarenethiolate.

Reaction of 2,3-dimethyl-1,4-naphthoquinone with an excess of sodium benzothiazole-2-thiolate in benzene–methanol for 19 h at room temperature followed by 4·5 h at 50 °C gave, besides the starting quinone and disulphide, a product (8%) $C_{20}H_{15}NO_3S_2$, yellow plates, m.p. 135—140 °C, showing $\lambda_{max}$ (EtOH) 247, 260, 294sh, and 358 nm (log $\epsilon$ 4·33, 4·21, 3·96, and 4·24); and $\nu_{max}$ (KBr) 1690br, 1640, and 1590 cm$^{-1}$. The molecular formula and principal mass spectral fragmentation [$m/e$ 381($M^+$, 0·8%), 215($M^+ - C_7H_4NS_2$, 100%)] confirm the presence of one mercaptobenzothiazole unit while the $^1H$ n.m.r. spectrum ($CDCl_3$) comprises one methyl ($\delta$ 1·66) and one methoxy (3·36) singlet, an aromatic complex (8 ArH), and a low-field singlet (1H) at $\delta$ 8·77. These data are consistent with structure (**4**) which was confirmed by $X$-ray crystallography.

*Crystal data:* $M$ = 381·5, monoclinic, $a$ = 9·143(3), $b$ = 23·919(6), $c$ = 8·498(3) Å, $\beta$ = 107·7(1)°, $U$ = 1770·5 Å$^3$, $D_c$ = 1·43, $D_m$ = 1·42 g cm$^3$, $Z$ = 4, $F$(000) = 792, space group $P2_1$. Mo-$K_\alpha$ radiation (graphite monochromator), $\lambda$ = 0·71069 Å, $\mu$ = 3·17 cm$^{-1}$. Intensities were measured out to $\theta < 27·5°$ and a total of 4191 reflections were scanned ($\omega$—$2\theta$ mode) of which 3271 had a net count of $>3\sigma(I)$ and were used in the refinement.†

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The structure was solved automatically at the first attempt using MULTAN 77 which revealed all but two of the **52** expected atoms. The missing two were readily located by Fourier methods. Refinement proceeded by full-matrix least-squares to convergence with isotropic temperature factors and then by blocked refinement in which each of the independent molecules comprised one block using anisotropic temperature factors. The hydrogen atoms were then located by a difference map and subsequently included (but not refined) in the computations. At convergence, the maximum shift/standard deviation was 0·1 and the conventional $R$ was 6·0%. The two independent molecules are related to a good approximation by a non-crystallographic centre of symmetry. After the structure refinement was completed in the space group $P2_1$ an attempt was made to refine the structure as $P\bar{1}$ with results which showed clearly that the original choice of space group had been correct. A perspective drawing of a single molecule is shown in the Figure.

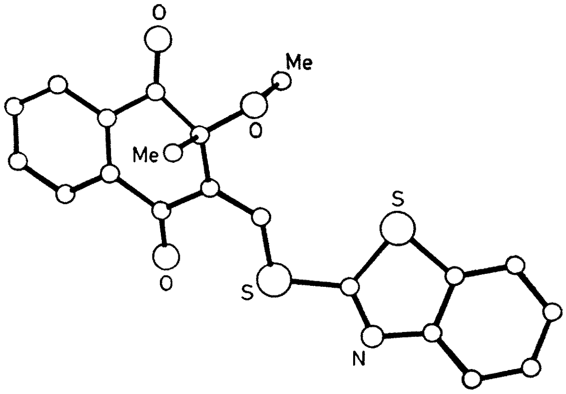

FIGURE. Perspective drawing of a single molecule of (**4**).

The reaction appears to proceed by nucleophilic addition of thiolate to a side-chain of 2,3-dimethyl-1,4-naphthoquinone (in the quinone-methide tautomeric form)[1] leading to (**1**; R = $C_7H_4NS$), followed by nucleophilic addition of methoxide ion ($ArS^- + MeOH \rightleftharpoons ArSH + MeO^-$) to the quinone ring to give (**3**) and subsequent oxidation.

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[1] R. H. Thomson and R. D. Worthington, *J. Chem. Soc., Perkin Trans.* 1, 1980, 282.