SYNTHESIS AND PROPERTIES OF BENZOANNELATED 6-(1,3-DITHIOLAN-2-YLIDEN)-2,4-CYCLOHEXADIEN-1-ONES*

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A general route to push-pull stabilized quinone methides starting from the corresponding phenols and proceeding *via* alkylation of aromatic hydroxy dithiocarboxylates has been used to synthesize the 1-oxo-2-(1,3-dithiolan-2-yliden)-1,2-dihydronaphthalene (*V*) and 9-oxo-10-(1,3-dithiolan-2-yliden)-9,10-dihydrophenanthrene (*VI*). In the case of α-naphthole, the reaction leads to a mixture of isomers with little preference shown for *para vs ortho*. The structures of the compounds are elucidated by their ^{1}H-NMR spectra.

It has been recognized for some time[1,2] that the replacement of exocyclic methylene hydrogens in *para* quinone methides by alkyl thio groups, *e.g.* as in *I*, markedly increases their stability. To explain this behaviour, a push-pull interaction between the dithiolane and carbonyl moieties was proposed. Similarly substituted quinone methides have received considerable attention in both reactivity studies[3,4] and spectroscopic investigations[5-8].

By contrast, rather little is known about the isomeric push-pull *ortho*-quinone methides. Although general synthetic methods leading to (1,3-dithiolan-2-yliden)-cyclohexadien-1-ones have been described[1,2] only one member of the *ortho*-family (*II*) has been prepared[2]. In this paper we attempted to prepare some new *ortho*-derivatives by using a versatile synthetic procedure[2] based on the reaction of corresponding phenolate anions with carbon disulphide. In the hope of obtaining both the *ortho*- and *para*-positional isomers, we used first phenol as a starting material. Unfortunately, all attempts to isolate *o*-dithiolane *III* failed. Instead, only *para*-isomer was produced, accompanied by a considerable amount of polymeric material. Based on analogy with the behaviour of *o*-thioquinone methide *IV* which was found to exist in solution only as an equilibrium mixture with its dimer[9,10], the above results were not surprising. Serious doubts may however be cast upon an earlier observation[2] claiming exclusively the formation of *para*-isomer when α-naphthole was treated in a similar manner (Scheme 1). Reproducing the described[2] experiments we were able to isolate two components after column chromatography of the crude

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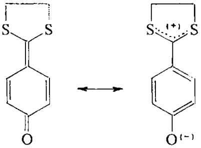
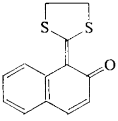


I



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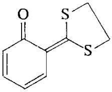

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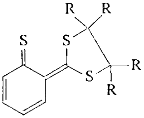

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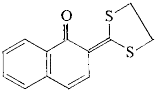

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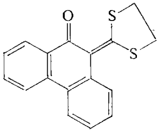
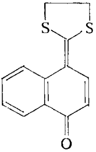
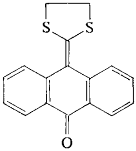


VI

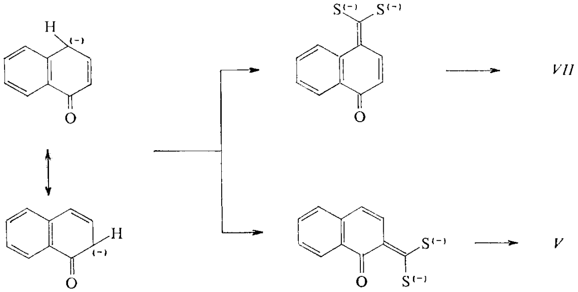


VII



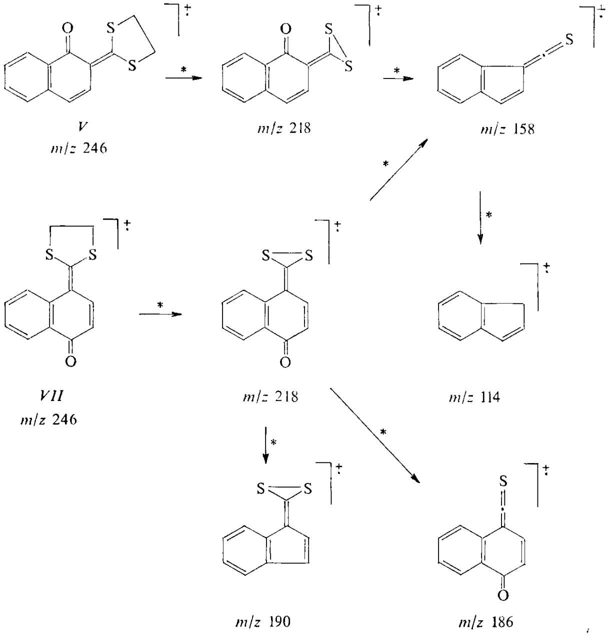
VIII

mixture. These compounds were shown by elemental analysis and mass spectrometry to be isomers of molecular formula $C_{13}H_{10}OS_2$ and on the basis of UV and IR spectra the isomers were tentatively assigned structures *V* and *VII*. The mass spectral



SCHEME 1

fragmentation patterns of both isomers *V* and *VII* were almost identical (Scheme 2). The spectrum of *V* is dominated by ion of *m/z* 158. Appropriate metastable peak suggested that it was formed, *via* ion *m/z* 218, by a successive loss of ethylene and COS. Ions of *m/z* 218 and 158 were observed in the spectrum of *VII* as well. In addition, ion *m/z* 218 generated from *VII* was a source of two other fragments: that of *m/z* 190 was due to a loss of CO from quinonoid ring, whereas loss of sulphur from dithiirane ring gave ion *m/z* 186.



SCHEME 2

Additional structural information was obtained from ^{1}H-NMR spectra (Table I). It is well known, that magnetic anisotropy of a carbonyl group in naphthoquinone, anthraquinone and phenanthraquinone is responsible for considerable downfield shift of *peri*-hydrogens in the substituted aromatic ring (*e.g.* $H_{(5)}$ and $H_{(8)}$ in naphtho-

TABLE I

^{1}H-NMR Chemical shifts and coupling constants of derivatives *I*, *II*, *V*—*VIII*

Compound	$I^{a,d}$	$II^{a,d}$	$V^{b,d}$	$VI^{c,d}$	$VII^{b,d}$	$VIII^{a,d}$
$C_{(1)}$—H	—	—	—	8·10—8·51	—	7·99 $J_{1,2}$ = 7·5 $J_{1,3}$ = 1·2
$C_{(2)}$—H	6·38 $J_{2,3}$ = 9·7	—	—	7·26—7·81	6·44 $J_{2,3}$ = 10·1 $J_{2,8}$ = 0·8	7·53 $J_{2,1}$ = 7·5 $J_{2,3}$ = 8·0 $J_{2,4}$ = 1·6
$C_{(3)}$—H	7·47 $J_{3,2}$ = 9·7	6·66 $J_{3,4}$ = 9·6	7·16 $J_{3,4}$ = 9·5 $J_{3,8}$ = 0·5	7·26—7·81	7·94 $J_{3,2}$ = 10·1 $J_{3,5}$ = 1·1	7·34 $J_{3\cdot 2}$ = 8·0 $J_{3,4}$ = 7·2 $J_{3,1}$ = 1·2
$C_{(4)}$—H	—	7·50 $J_{4,3}$ = 9·6	6·70 $J_{4,3}$ = 9·5 $J_{4,6}$ = 0·7 $J_{4,8}$ = 0·9	8·10—8·51	—	8·14 $J_{4,3}$ = 7·2 $J_{4,2}$ = 1·6
$C_{(5)}$—H	7·47 $J_{5,6}$ = 9·7	7·50 $J_{5,6}$ = 7·9 $J_{5,8}$ = 0·6	7·44 $J_{5,6}$ = 8·2 $J_{5,8}$ = 0·6	8·10—8·51	8·34 $J_{5,6}$ = 8·2 $J_{5,7}$ = 1·1 $J_{5,8}$ = 0·6 $J_{5,3}$ = 1·1	8·14 $J_{5,6}$ = 7·2 $J_{5,7}$ = 1·6
$C_{(6)}$—H	6·38 $J_{6,5}$ = 9·7	7·29 $J_{6,5}$ = 7·9 $J_{6,7}$ = 6·7 $J_{6,8}$ = 1·3	7·56 $J_{6,5}$ = 8·2 $J_{6,7}$ = 6·6 $J_{6,8}$ = 1·6 $J_{6,4}$ = 0·7	7·26—7·81	7·65 $J_{6,5}$ = 8·2 $J_{6,7}$ = 7·1 $J_{6,8}$ = 1·6	7·34 $J_{6,5}$ = 7·2 $J_{6,7}$ = 8·0 $J_{6,8}$ = 1·2
$C_{(7)}$—H	—	7·50 $J_{7,6}$ = 6·7 $J_{7,8}$ = 8·2	7·41 $J_{7,6}$ = 6·6 $J_{7,8}$ = 7·9	7·26—7·81	7·46 $J_{7,6}$ = 7·1 $J_{7,8}$ = 7·9 $J_{7,5}$ = 1·1	7·53 $J_{7,6}$ = 8·0 $J_{7,8}$ = 7·5 $J_{7,5}$ = 1·6
$C_{(8)}$—H	—	8·31 $J_{8,7}$ = 8·2 $J_{8,6}$ = 1·3 $J_{8,5}$ = 0·6	8·41 $J_{8,7}$ = 7·9 $J_{8,6}$ = 1·6 $J_{8,5}$ = 0·6 $J_{8,3}$ = 0·5 $J_{8,4}$ = 0·9	8·10—8·51	8·36 $J_{8,7}$ = 7·9 $J_{8,6}$ = 1·6 $J_{8,5}$ = 0·6 $J_{8,2}$ = 0·8	7·99 $J_{8,7}$ = 7·5 $J_{8,6}$ = 1·2

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[a] 100 MHz data; [b] 200 MHz data; [c] 60 MHz data; correct values of δ and J could not be determined; [d] S—CH_2—CH_2—S protons; *I*: 3·67 s; *II*: 3·31—3·55 m; *V*: 3·43—3·61 m; *VI*: 3·43 s; *VII*: 3·51 m (2 H), 3·74 m (2 H); *VIII*: 3·29 s

quinone, as well as $H_{(1)}$ and $H_{(8)}$ in phenanthraquinone, are located at δ 8·07, whereas $H_{(1)}$, $H_{(4)}$, $H_{(5)}$ and $H_{(8)}$ in anthraquinone are somewhat displaced to δ 8·31). Similar downfield shift (probably of more complex origin) exerted 1,3-dithiolanylidene group in quinone methides *II*, *VI* and *VIII*. In the case of naphthalene derivative *II* the singlet at δ 8·31 was attributed to $H_{(8)}$ and in anthracene derivative *VIII* *peri*-hydrogens $H_{(1)}$ and $H_{(8)}$ resonated at δ 7·94. In critical region of poorly resolved spectrum of phenanthrene derivative *VI* a resonance of δ 8·10–8·15 appeared which, with certain caution, could be ascribed to $H_{(1)}$. Examination of ^{1}H-signals for quinone methide *VII* demonstrated that resonances of both $H_{(5)}$ and $H_{(8)}$ were subjected to *peri*-effect (δ 8·34 and 8·36, respectively). This finding is compatible only with 1,4-substitution in naphthalene skeleton. On the contrary, in the spectrum of quinone methide *V* only $H_{(8)}$ signal was shifted downfield, whereas $H_{(5)}$ resonated at δ 7·44. These data, which may be correlated with those of the compound *II*, suggest 1,2--substitution in naphthalene skeleton.

It should be noted that there was considerable discrepancy between the m.p. of *VII* (135–137°C) and that reported (177°C)[2]. Similar discrepancy exists also between our and previously presented[2] UV data in methanol (428 nm, 330 nm, 310 nm *vs* 482 nm, 457 nm, 434 nm, 322 nm and 310 nm). Therefore, the structure of *VII* was additionally confirmed by converting the compound to the known[10] ethyl ester (see Experimental) *via* the 4-hydroxynaphthalene-1-carboxylic acid. Thus, *VII* must indeed have the structure assigned and the earlier reported data have to be revised. The source of the m.p. and UV discrepancies remains unresolved.

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. Analytical samples were dried at room temperature and 13 Pa for 7 h. The IR spectra were measured in chloroform on Perkin Elmer 580 spectrophotometer in a 0·1 mm cell. Mass spectra were taken on an AEI MS902 mass spectrometer (70 eV; source temperature 110–230°C). ^{1}H-NMR spectra were measured on spectrometers Tesla BS-467 (at 60 MHz), Varian HA-100 (at 100 MHz) and Varian XL-200 (at 200 MHz) in deuteriochloroform with tetramethylsilane as internal reference. Both the chemical shifts and coupling constants were obtained by first-order analysis.

1-*Oxo*-2-(1,3-*dithiolan*-2-*yliden*)-1,2-*dihydronaphthalene* (V). Starting from α-naphthole, the general procedure *A* as described in ref.[2] was followed except that two components were isolated after column chromatography of the crude product over neutral activity II alumina (eluent chloroform). The early fractions provided *V* as orange red crystals (19%), m.p. 121·5°C (methanol). For $C_{13}H_{10}OS_2$ (246·3) calculated: 63·36% C, 4·09% H, 26·03% S; found: 63·20% C, 4·12% H, 25·89% S. IR spectrum (chloroform): 1 619·0 cm^{-1} (C=O). UV spectrum (methanol): 487 nm (sh), 461 nm, 439 nm (sh), 411 nm (sh, w). Mass spectrum: 246 ($M^{+\cdot}$). The later fractions gave 1-oxo--4-(1,3-dithiolan-2-yliden)-1,4-dihydronaphthalene (*VII*) as an orange yellow solid (24%) m.p. 135–137°C (ethyl acetate). For $C_{13}H_{10}OS_2$ (246·3) calculated: 63·36% C, 4·09% H, 26·03% S; found: 63·28% C, 4·13% H, 25·99% S. IR spectrum (chloroform): 1 625·5 cm^{-1} (C=O). UV spectrum (methanol): 427 nm. Mass spectrum: 246 ($M^{+\cdot}$).

9-*Oxo*-10-(1,3-*dithiolan*-2-*yliden*)-9,10-*dihydrophenanthrene* (VI). The procedure was exactly the same as that described above except that 9-hydroxyphenanthrene[11] was used as starting phenol to give *VI* (62%), m.p. 174—176°C (chloroform–hexane). For $C_{17}H_{12}OS_2$ (294·4) calculated: 68·89% C, 4·08% H, 21·64% S; found: 68·68% C, 4·01% H, 21·50% S. IR spectrum (chloroform): 1 621·5 cm^{-1} (C=O). UV spectrum (methanol): 433 nm, 419 nm, 362 nm. Mass spectrum: 296 ($M^{+\cdot}$).

Oxidative cleavage of VII. Hydrogen peroxide (30%, 3 ml) was added dropwise to a stirred solution of *VII* (1·23 g) in acetic acid (30 ml) at 60°C. The mixture was cooled and slowly poured into ice water. The white solid was filtered off and dissolved in dichloromethane. After washing with water and drying ($MgSO_4$), the organic layer was evaporated and the residue was esterified by ethanol–hydrogen chloride reagent to yield ethyl 4-hydroxynaphthalene-1-carboxylate (87%), m.p. 132—133°C (ref.[12] m.p. 134°C). IR spectrum (chloroform): 1 695 cm^{-1}, 1 242 cm^{-1} ($COOC_2H_5$), 3 601 cm^{-1} (OH). Mass spectrum: 216 ($M^{+\cdot}$).

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