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REACTIONS OF BENZO-1,2-DITHIOLE-3-THIONE WITH N,N'-DIALKYL-1,2-DIAMINOETHANES. SYNTHESIS OF o-THIOQUINONEMETHIDES WITH A KETENE AMINAL GROUP

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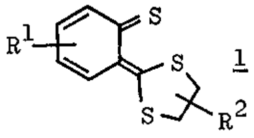
Benzo-1,2-dithiole-3-thione (2) reacted with N,N'-dialkyl-1,2-diaminoethanes (3) to give o-thioquinonemethides with a ketene aminal group (4-6) in high yields, which were found to be of considerable betain nature significantly different from previously known o-thioquinonemethides with a ketene thioacetal group (1).

Synthesis of o-thioquinonemethides (1) from the photoreaction of 1,2-dithiole-3-thiones with olefins has recently been reported by de Mayo[1] and by us.[2]

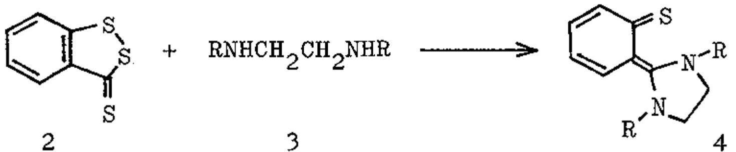


1

R^1=H or $(CH=CH)_2$
R^2=Alkyl

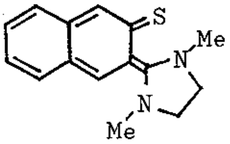
We now describe another type of o-thioquinonemethides (4) with a ketene aminal group which show significantly different properties from 1.

Reaction of benzo-1,2-dithiole-3-thione (2) with N,N'-dialkyl-1,2-diaminoethane (3) in ethanol afforded 4 in high yields. In the reaction of 2 with 3a, the formation of hydrogen sulfide (91% as PbS) and sulfur (94%) was also confirmed. Thioquinonemethides (5) (78%) and (6) (85%) were also prepared in a similar way from the corresponding 1,2-dithiole-3-thiones. Compound 7 (65%) was synthesized by the reaction of more reactive dithiolium salt (8)[3] with N,N'-dimethyl-o-phenylenediamine using ion exchange resin as base.



2 3 4

a:	R=Me	reflux, 4h	99%	mp 153-5°C
b:	R=Et	reflux, 6h	64%	mp 148-9°C
c:	R=i-Pr	160 °C, 30h (sealed tube)	78%	



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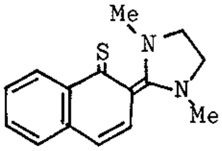

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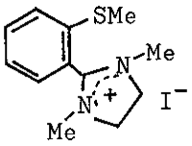

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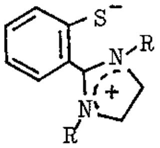

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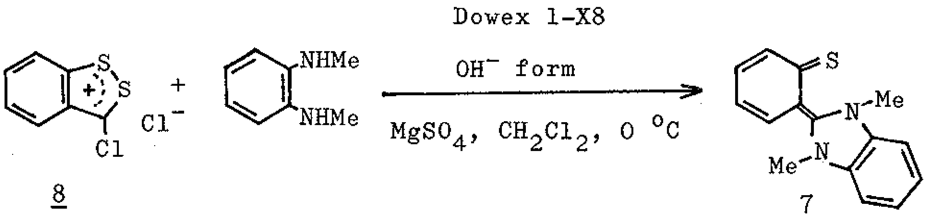


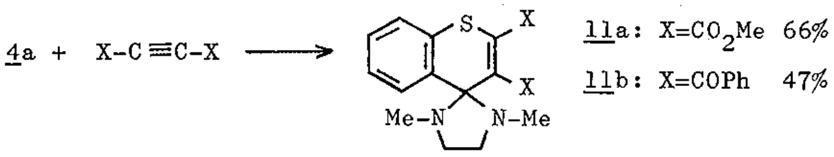
8 7

The electronic spectra of 4b[4] showed no concentration dependence, indicating it exists as monomer in solution. This is in marked contrast with 1 which is in equilibrium with a dimer.[1,2] The NMR spectra of 4-7 are very similar to each other, implying other thioquinonemethides synthesized here are also monomeric in solution. Of particular interest is the isolation and stability of 5 since compounds with 2,3-naphthoquinone structure are usually very unstable[5] and isolable only in special cases.[6] The NMR chemical shifts (CD_3OD) of N-methyl protons of 4a, 5, and 6 (δ 2.90-2.92) are almost the same as that of 9 (δ 2.92; prepared from 4a and methyl iodide) and those of ethylene protons (δ 4.00-4.06) are fairly close to that of 9 (δ 4.14), indicating the large contribution of ionic canonical structure (e.g. 10 for 4) in these thioquinonemethides. This is reflected in the solubility of these compounds; for instance, 4a is very soluble in water and alcohols but only slightly soluble in chloroform and benzene.

The importance of the ionic contribution 10 to the ground state of 4 was also shown by solvent effect of the UV spectra of 4b.[3] The more polar is the solvent, the shorter becomes the absorption maximum, implying the stabilization of the ionic ground state by polar solvents. Here again, the thioquinonemethides with a ketene aminal group are quite different from those with a ketene thioacetal group (1) whose electronic spectra show no essential solvent dependence.

Compound 4a reacted with dimethyl acetylenedicarboxylate and dibenzoylacetylene in acetonitrile at room temperature to give

[4+2] adduct (11), suggesting a possible route to six-membered sulfur heterocycles.



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4 Solvent, λ_{max} (nm), log ε: H_2O, 252, 4.00; EtOH, 278, 4.18; MeCN, 299, 4.26; CH_2Cl_2, 299, 4.06; PhH, 307, 4.27.

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