CHEMISTRY LETTERS, pp. 287-288, 1977. Published by the Chemical Society of Japan

7,10-DITHIASESQUIFULVALENE-1,6-QUINONE
[2-(1,3-DITHIOL-2-YLIDENE)-4,6-CYCLOHEPTADIENE-1,3-DIONE]

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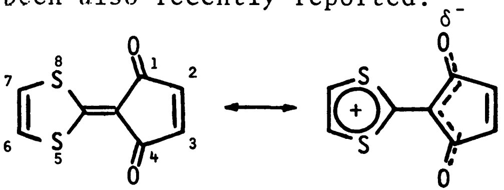
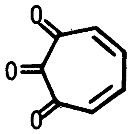
The title compound was synthesized by the condensation of 3-hydroxytropone with 2-methylthio-1,3-dithiolylium iodide and its spectroscopic properties were described.

Very recently we have reported the synthesis of thermally stable 5,8-dithiafulvalene-1,4-quinone (1), whose ground state is well represented as a hybrid of structures 1a and 1b.1) This paper is concerned with the synthesis of 7,10-dithiasesquifulvalene-1,6-quinone [2-(1,3-dithiol-2-ylidene)-4,6-cycloheptadiene-1,3-dione] (4), which is a vinylog of 1 and corresponds to a quinone methide type of a derivative of *o*-tropoquinone (2).2) The synthesis of derivatives of 3, an isomer of 4, has been also recently reported.3)



1a 1b

1



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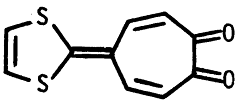

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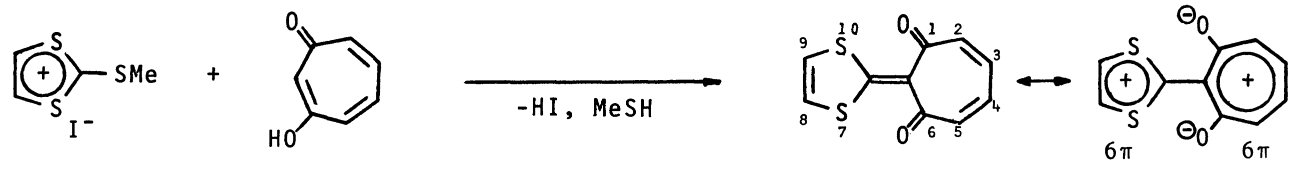
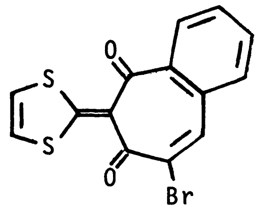
Heating the iodide 54) with 3-hydroxytropone (6)5) in boiling acetonitrile in the presence of pyridine for 4.5 h gave the quinone 4 in 59% yield: mp 207-208°C (from acetonitrile, orange needles); $\nu_{C=O}^{KBr}$ 1505 cm^{-1}; $\lambda_{max}^{CHCl_3}$ 446 nm (log ε 4.05), 425 (4.08), and 342 (3.31) and λ_{max}^{EtOH} 441 nm (log ε 4.11), 423 (4.14), 329 (3.30), and 276 (4.06); δ (DMSO-d_6, 110°C) 8.12 (2H, s, -S-C$\underline{H}$=C$\underline{H}$-S-) and 6.7-7.0 (4H, AA'BB' m, -C$\underline{H}$=C$\underline{H}$-C$\underline{H}$=C$\underline{H}$-). Found: S, 28.54%. Calcd for $C_{10}H_6O_2S_2$: S, 28.81%. 2,3-Benzo-5-bromo-7,10-dithiasesquifulvalene-1,6-quinone (7), a benzo-derivative of 4, was also prepared in 75% yield by the condensation of 5 with the benzotropone 86) in boiling acetonitrile: mp 186-189°C (from acetonitrile, yellow needles); $\nu_{C=O}^{KBr}$ 1525 cm^{-1}; $\lambda_{max}^{CHCl_3}$ 426 nm (log ε 4.29), 412 sh (4.25), and 311 (4.04) and λ_{max}^{EtOH} 423 nm (log ε 4.27), 405 (4.27), and 310 (4.04); δ ($CDCl_3$) 7.4-7.8 (4H, complex m, benzene ring protons), 7.79 (2H, s, -S-C$\underline{H}$=C$\underline{H}$-S-), and 8.11 (1H, s, seven-membered ring proton). Found: S, 18.07%. Calcd for $C_{14}H_7BrO_2S_2$: S, 18.26%.

For comparison with 4 and 7, 2-(1,3-dithiolan-2-ylidene)-4,6-cycloheptadiene-1,3-dione (9) was prepared in 47% yield by the reaction of 6 with the methylsulfate 107) in boiling acetic acid in the presence of pyridine: mp 124-126°C (from carbon tetrachloride, orange granules); $\nu_{C=O}^{KBr}$ 1535 cm^{-1}; $\lambda_{max}^{CHCl_3}$ 392 nm (log ε 3.96) and



5 6 4a 4 4b



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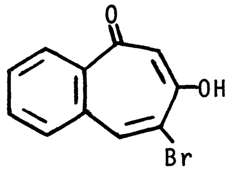

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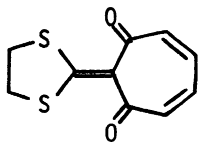

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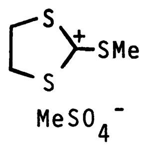

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370 sh (3.94) and λ_{max}^{EtOH} 390 nm (log ε 4.13); δ ($CDCl_3$) 3.32 (4H, s, $-S-CH_2-CH_2-S-$) and 6.4-7.0 (4H, AA'BB' m, -CH=CH-CH=CH-). Found: S, 28.46%. Calcd for $C_{10}H_8O_2S_2$: S, 28.55%.

Compounds 4 and 7 thus obtained are thermally stable, but compound 9 appreciably polymerized when heated in carbon tetrachloride.

The saturation of the C_8-C_9 double bond of 4 results in a high-frequency shift of the carbonyl absorption and a hypsochromic shift of the UV absorption maximum; the carbonyl frequencies of 4 and 9 appear at 1505 and 1535 cm^{-1}, respectively and the longest absorptions of the UV spectra of 4 and 9 in chloroform occur at 446 and 392 nm, respectively. These data indicate that the C_8-C_9 double bond of 4 enters into a cyclic conjugated system as observed with 1. Even more impressive is the anomalously low carbonyl frequency of 4. It is lower than that of 1 by 142 cm^{-1}.[8] This may be mainly attributed to the pronounced contribution of the polar structure 4b to the ground state of 4. Stabilization due to two aromatic sextets makes 4b favourable. This type of stabilization is lacking in 1. Further support for this description is found in the NMR spectrum. The dithiole ring protons of 4 resonate at δ 8.12 in DMSO-d_6 at 110°C, which is lower than those of 1 by 0.60 ppm under the same conditions. This chemical shift value is rather near to that of the C_4 and C_5 protons of the iodide salt 5, δ 8.65 in CF_3CO_2D, thus suggesting the electron deficient nature of the five-membered ring, i.e., the pronounced contribution of 4b.

References and Notes

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(Received January 31, 1977)