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PHOTOREACTION OF NAPHTHO-1,2-DITHIOLE-3-THIONES WITH CYCLOHEXENE. ISOLATION OF A STABLE o-THIOQUINONEMETHIDE AND AN EQUILIBRIUM WITH [4+2] DIMER[1)]

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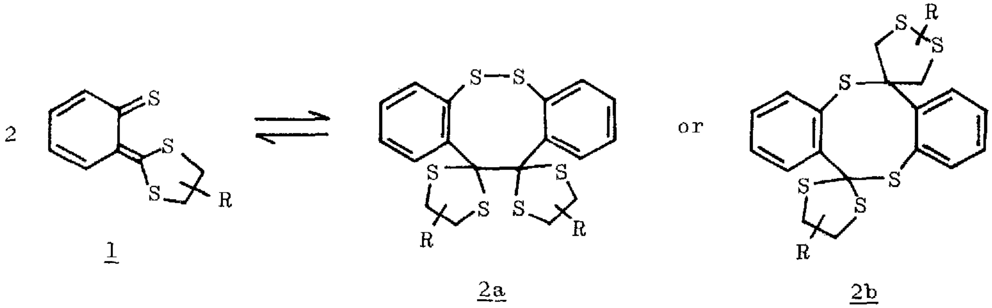
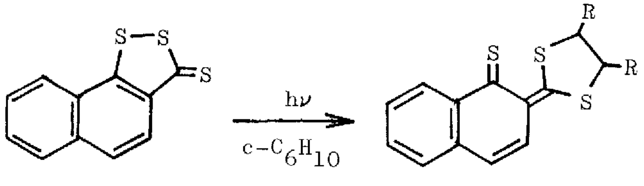
Chemistry of o-quinonoid compounds has been a subject of continuing interest in recent years.[2)] de Mayo et al.[3)] and we[4)] have recently reported the photochemical formation of o-thioquinonemethides 1 and their equilibrium with [4+4] dimers 2a or 2b (presumably 2a). The dimer 2 was obtained as white crystals, but the pure monomer 1 could not be isolated although its existence in solution was established by the spectroscopic data and chemical reactions.



We now wish to report the isolation of a monomeric o-thioquinonemethide and a thermal equilibrium with [4+2] dimer in the corresponding naphtho derivatives.

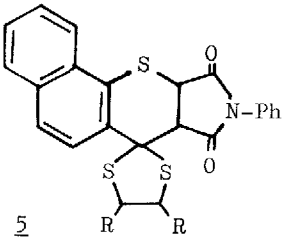
Irradiation[5)] of naphtho[2,1-d]-1,2-dithiole-3-thione 3[6)] in the presence of cyclohexene afforded o-thioquinonemethide 4 as deep purple crystals in a quantitative yield.[7)] The monomeric nature of 4 was established by molecular weight determination[8)] (found 319; calcd 316.5) and by UV spectrum ($\lambda_{max}^{CH_2Cl_2}$ 323 (ε 24300), 353 (10800), 392sh (2540), and 540 nm (11800)) which showed no concentration dependence. This represents the first example of isolation of o-thioquinonemethide. Upon reaction with N-phenylmaleimide, 4 gave 1:1 adduct 5 in 83% yield.

Photoreaction[5] of naphtho[1,2-d]-1,2-dithiole-3-thione 6[6] with cyclohexene led to a deep red solution, the TLC of which showed the presence of a single product together with a small amount of the starting thione 6. The addition of N-phenylmaleimide to the reaction solution afforded 1:1 adduct 9 (54%), the identity of the red compound as 7 thus being established. Purification of the reaction mixture by dry column chromatography (silica gel, CCl_4) to remove 6, however, resulted in the formation of a yellow crystalline compound 8 besides the red compound 7 (total yield 95%).[9] The yellow compound free from 7 was obtained by TLC purification[10] and was identified as a dimer of 7 on the basis of molecular weight determination[8] (found 666, calcd 633) and its reversion to 7



RR = -$(CH_2)_4$-

3 4



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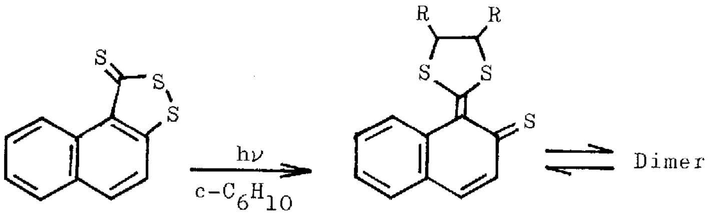

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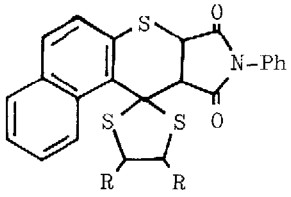

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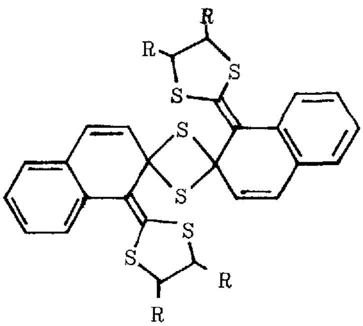

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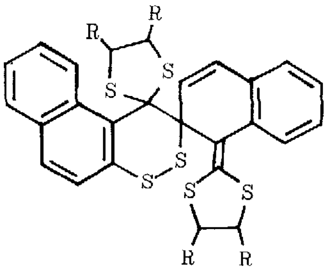

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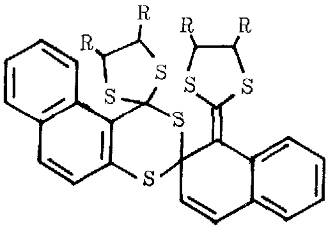

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by heating. The benzene solution of 8 and N-phenylmaleimide, on heating at about 60°, gave 9 in 64% yield.

Of many possible structures of the dimer 8, [4+4] adduct like 2 and [2+2] adducts other than 10 can be eliminated by the electronic spectrum ($\lambda_{max}^{CH_2Cl_2}$ 263 (ε 19400), 354sh (4650), and 450 nm (9540)), because the former has only naphthalene chromophore which should not show any strong band above 350 nm and any of the latters has a conjugate thione system which would have an absorption above 570 nm.11) Structure 10 can be ruled out by the NMR spectrum with intensity ratio of the aromatic to the olefinic protones of 10:2.10) Thus, the dimer must be [4+2] adduct 11 or 12 although we do not have experimental evidence at present enabling us to conclude which is correct. The mutual conversion between 7 and 8 is the first example of a reversible thermochromic system where both monomeric and dimeric o-quinonoid compounds can be isolated.12)

The foregoing interesting contrast in behavior of 7 with isomeric thioquinonemethide 4 probably results from the lesser stability of the monomer 7 because of interaction between the ketene thioacetal group and the hydrogen at peri position.

The difference in structure of the dimers (i.e. [4+4] vs. [4+2]) between the benzo 1 and the naphtho system 7 may also be attributed to strong steric interaction between the dithiolane ring and the fused aromatic ring in [4+4] adduct of the latter as clearly suggested by inspection of the molecular model.

References and Notes

1) Part IV of a series on conjugated ketene thioacetals. For part III see: R. Okazaki, M. O-oka, and N. Inamoto, J.C.S. Chem. Comm., 1976, in press.

2) For recent reviews, see R. Gompper, Angew. Chem. Int. Ed. 8, 312 (1969); H.U. Wagner and R. Gompper, "The Chemistry of the Quinonoid Compounds," Ed. by S. Patai, Chapter 18, John Wiley & Sons, 1974; R. Okazaki, Yuki Gosei Kagaku Kyokaishi, 34, 439 (1976).

3) P. de Mayo and H.Y. Ng, J.C.S. Chem. Comm., 877 (1974).

4) R. Okazaki and N. Inamoto, Chem. Letters, 1439 (1974).

5) In benzene using Pyrex-filtered light from 100W medium pressure mercury lamp for 1 hr.

6) L. Legrand, Bull. Soc. Chim. France, 1599 (1959).

7) Compound 4: m.p. 153.8-155.3° (dec); NMR ($CDCl_3$) δ 1.1-2.3(m, 8H), 3.7-4.2 (m, 2H), 6.97, 7.13(A part of AB quartet, 1H), 7.60, 7.76(B part of AB quartet), and 7.42-7.53(m, 4H in total), 8.8-9.0(m, 1H).

8) Vapor pressure osmometry in benzene at 40°.

9) A sample rich in the yellow compound 8 could also be obtained by heating the solution of the red compound 7 at about 60° and subsequent cooling. Therefore, attempts to obtain pure 7 by TLC or recrystallization always resulted in the formation of the yellow compound, thus precluding us to get pure 7 so far. The spectral data of almost pure 7 were as follows: UV (CH_2Cl_2) 235(ε 23900), 263(17800), 295(12100), 327(7160), 392sh(3170), 412 (4440), and 496 nm(4630); NMR($CDCl_3$) δ 1.0-2.2(m, 8H), 3.4-3.9(m,2H), 7.1-7.6(m, 5H), and 8.2-8.4(m, 1H).

10) Compound 8: m.p. 119-121° (dec); NMR ($CDCl_3$) δ 1.0-2.5(m, 16H), 3.5-4.2 (m, 4H), 6.74, 6.89(A part of AB quartet, 1H), 7.48, 7.63(B part of AB quartet), and 7.2-8.1(m, 11H in total).

11) Cf. D.H.R. Barton, L.L. Choi, R.H. Hesse, M.M. Pechet, and C. Wilshir, J.C.S. Chem. Comm., 557 (1975).

12) Dimerization of unstable o-quinonoid compounds into their [4+2] dimers has been reported. For example: C.R. Flynn and J. Michl, J. Am. Chem. Soc., 96, 3280 (1974); J. Bornstein, J.E. Shields, and J.H. Supple, J. Org. Chem., 32, 1499 (1967); M.S. Chanhan, F.M. Dean, D. Matkin, and M.L. Robinson, J. Chem. Soc. Perkin I, 120 (1973); G. Catterall, J.C.S. Chem. Comm., 41 (1974).