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o-THIOQUINOMETHIDES. PREPARATION AND THE EQUILIBRIUM WITH THE [4+4] DIMER

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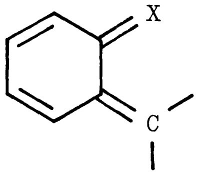
Photochemical reactions of 4,5-benzo-1,2-dithiole-3-thione with cycloalkenes afforded deep blue o-thioquinomethides which are in thermal equilibrium with the colorless dimers.

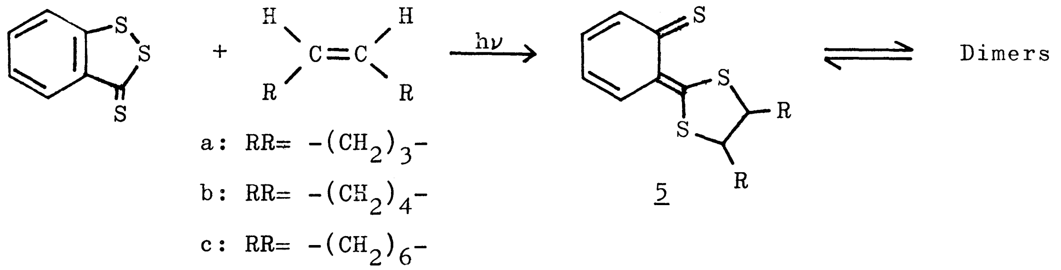
o-Quinodimethanes (1),[1] o-quinomethides (2),[2] and o-quinomethidimines (3)[3] have been of considerable interest in recent years because of their intriguing chemical and physical properties.[4] As for o-thioquinomethides (4), however, only the transient intermediacy has been reported.[5]

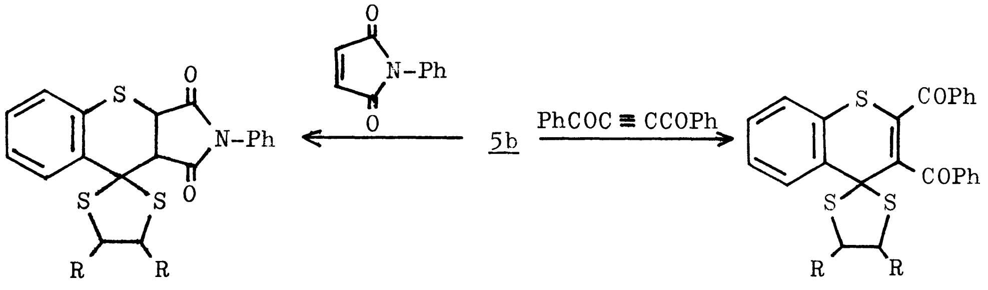


1: X=CR_2
2: X=O
3: X=NR_2
4: X=S

We now wish to report the first example of a stable o-thioquinomethide and its thermal equilibrium with the [4+4] dimer.[6] Ready access to the thioquinomethide was provided by application of the reported photoreaction[7] of aryl substituted 1,2-dithiole-3-thiones with olefins to 4,5-benzo-1,2-dithiole-3-thione.

Irradiation[8] of the benzodithiolethione in ether or benzene in the presence of olefins (cyclopentene, cyclohexene, and cyclooctene) afforded deep blue thiones (5) in about 90% yields. The structure of 5[9] was established by the reactions with N-phenylmaleimide and dibenzoylacetylene leading to Diels-Alder type addition products (6) and (7), respectively;[9] these reactions occured almost instantaneously at room temperature, suggesting 5 might act as a highly reactive 1,4-dipolar species.





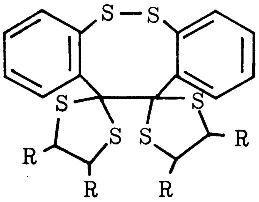
6 mp 218°C

7 mp 183°C

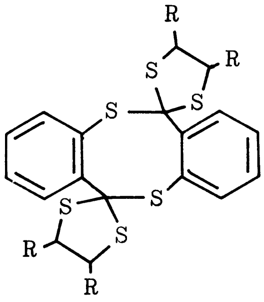
The color in solution of these adducts (5) are dependent on the solvent; 5b, for instance, is deep blue in dichloromethane and tetrahydrofuran but colorless in cyclohexane at room temperature. When 5b was recrystallized from carbon tetrachloride at -26°C, white crystals were obtained. Similar white crystals precipitated from fairly concentrated solution in tetrahydrofuran or dichloromethane shortly after the preparation of the solution. The colorless crystals thus obtained gave a deep blue solution upon dissolution in appropriate solvents. The colorless cyclohexane solution of 5b turned deep blue when heated at 80°C for several seconds and again became colorless upon standing at room temperature. Similar reversible change in color was also observed upon irradiation but prolonged irradiation caused a reaction leading to irreversible decomposition. These observations as well as concentration-dependent electronic spectra of these adducts suggested the existence of an equilibrium between the deep blue monomer and a colorless associated species. That the association is dimeric was shown by cryoscopic determination of the molecular weight in cyclohexane for the cyclohexene adduct (found: 542, calcd: 532).9)

Of many possible structures of the dimer, three types, *i.e.* [2+2], [2+4], and [4+4] dimers derived from addition involving the thiocarbonyl and the ketene-thioacetal functionalities, deserve serious consideration. Two of them, [2+2] and

[2+4] dimers,[10] can be ruled out by the UV spectra of the dimer which is essentially below 300nm,[9] because all of them must have either a triene containing ketenethioacetal which would have a strong absorption above 300nm[11] or a conjugated thione which should be colored. Thus, the dimer should be a [4+4] adduct, 8 or 9.



8



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Raney-nickel desulfurization[12] of the adduct with cyclohexene gave bibenzyl (5%) along with toluene (41%). Although the existence of the equilibrium and the potentially higher reactivity of the monomer prevent us from obtaining conclusive evidence for the structure of the dimer at present, we consider that the formation of bibenzyl suggests the structure 8. Facile dissociation into the monomer also appears to be in favor of 8 in view of the thermally and photochemically vulnerable disulfide bond.

Attempts to get conclusive evidence for the structure of the dimer and some reactions using highly polarizable thiones 5 are currently in progress.

References and Footnotes

1) C.R. Flynn and J. Michl, J. Amer. Chem. Soc., 95, 5802 (1973) and references cited therein.

2) R. Gompper and E. Kutter, Chem. Ber., 98, 1365, 1374 (1965); D.L. Coffen and P.E. Garrett, Tetrahedron Lett., 2043 (1969); see also A. Padwa and G.A. Lee, J. Amer. Chem. Soc., 95, 6149 (1973) and references cited therein.

3) R. Gompper and H.-D. Lehmann, Angew. Chem., 80, 38 (1968).

4) For a review in this area, see R. Gompper, Angew. Chem. Internat. Ed., 8, 312 (1969).

5) G. Jacqmin, J. Nasielski, G. Billy, and M. Remy, Tetrahedron Lett., 3655 (1973); see also O.L. Chapman and C.L. McIntosh, J.Amer. Chem. Soc., 92, 7001 (1970).

6) Similar results have been obtained by de Mayo's group of the University of Western Ontario for cyclopentene and tetramethylethylene adducts (Chem. Commun. 1974, in press). We thank Professor P. de Mayo for sending us the manuscript prior to publication.

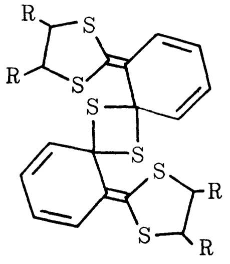
7) R. Okazaki, F. Ishii, K. Ozawa, and N. Inamoto, Chem. Lett., 9 (1972); R. Okazaki, F. Ishii, K. Okawa, K. Ozawa, and N. Inamoto, J. Chem. Soc. Perkin I, in press; P. de Mayo and H.Y. Ng, Tetrahedron Lett., 1671 (1973).

8) 100W medium pressure mercury lamp under nitrogen through pyrex for 45 min.

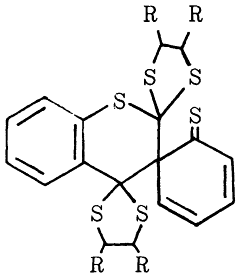
9) All new compounds (except for monomers 5a-c) were analyzed satisfactorily and gave spectral data in agreement with the proposed structures. For instance, 5b, mp 166-167°C (dec); NMR (carbon tetrachloride, -20°C, where the adduct is essentially dimeric): τ 2.02-2.84(m, 2H), 2.84-3.26(m, 2H), 5.50-5.90(m, 1H), 5.95-6.60(m, 1H), and 7.3-9.0(br, 8H); UV λ_{max} (cyclohexane, 0.628×10^{-4} M as a dimer, at 7°C, where it is colorless and hence essentially dimeric) 260nm (ε 1.04×10^{4}), λ_{max} (dichloromethane, 1.24×10^{-4} M as a monomer, at 23°C, where it is supposed to be mostly, though not completely, monomeric) 269 (1.09×10^{4}), 351 (4.05×10^{3}), and 584 (2.61×10^{3}).

10) For example,

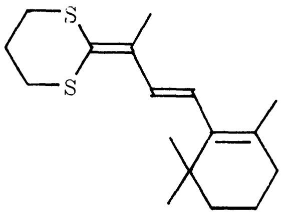
[2+2] dimer



[2+4] dimer



11) The UV spectrum of triene i has been reported to be λ_{max} 312nm (ε 22,700) (D. Seebach, M. Kolb, and B.-T. Gröbel Chem. Ber., 106, 2277 (1973)).



i

12) Tetrahydrofuran solution under reflux for 3 hr using W-4 Raney-nickel. The reaction was slow at room temperature. Toluene and bibenzyl were analyzed by high speed liquid chromatography.

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