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UNUSUAL MODE OF DIMERIZATION OF o-THIOQUINONE METHIDE. ISOLATION OF HEAD-TO-HEAD AND HEAD-TO-TAIL DIMERS

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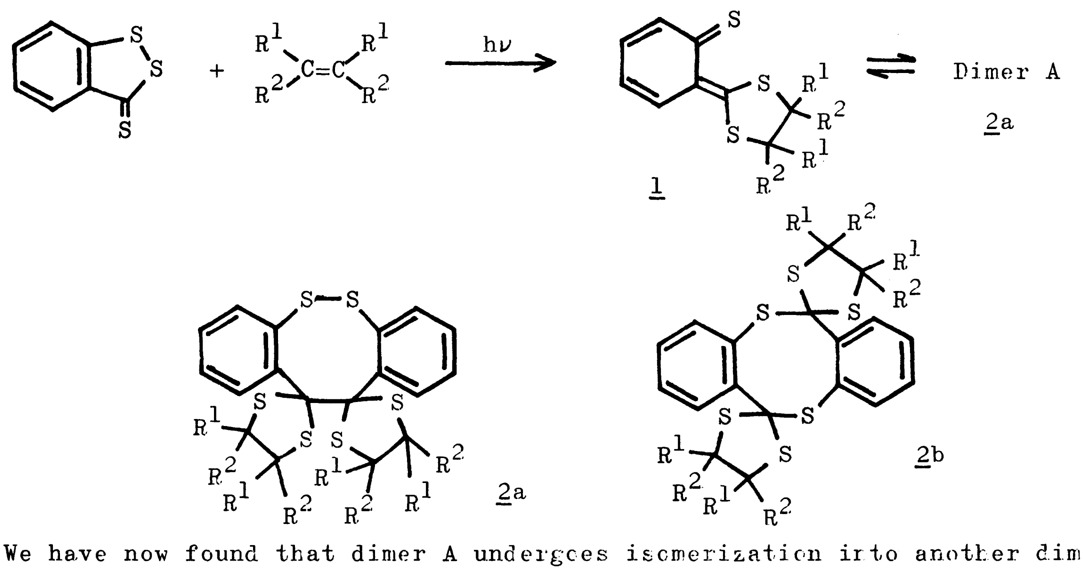
Reaction of o-thioquinone methide (1, $R^1=R^2=CH_3$) with 2-dimethylamino-3-methyl-1-butene afforded a head-to-tail [4+4] dimer of 1 (2b, $R^1=R^2=CH_3$). Photoreaction of naphtho[2,3-c][1,2]dithiole-3-thione with cyclohexene is also described.

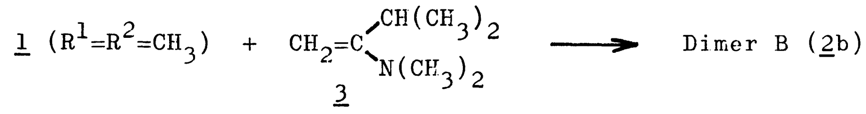
Of some interesting reactivities of o-quinonoid compounds, which have been a subject of intensive studies in recent years,$^{1)}$ most characteristic is their cycloaddition reaction. They react with dienophiles in a Diels-Alder fashion to give otherwise difficultly obtainable compounds,$^{2)}$ while, in the absence of dienophiles, they usually dimerize to afford [4+2] and/or [4+4] dimers, the mode of the dimerization being an intriguing manifestation of the nature of the o-quinonoid compounds.

We wish herein to report interesting observations concerning the dimerization of o-thioquinone methide. de Mayo$^{3)}$ and we$^{4)}$ previously described formation of the first stable o-thioquinone methide (1) by photoreaction of benzodithiolethione with olefins. The thione (1) was found to exist in solution as an equilibrium mixture with a dimer (designated as dimer A hereafter), but conclusive evidence for the structure could not be obtained although spectral data indicate that it must be a [4+4] dimer, 2a or 2b.



We have now found that dimer A undergoes isomerization into another dimer (designated as dimer B) under some special conditions. This fact enables us to determine unequivocally the structure of the both dimers and to compare the mode of dimerization for 1 with that for other types of o-quinonoid compounds.

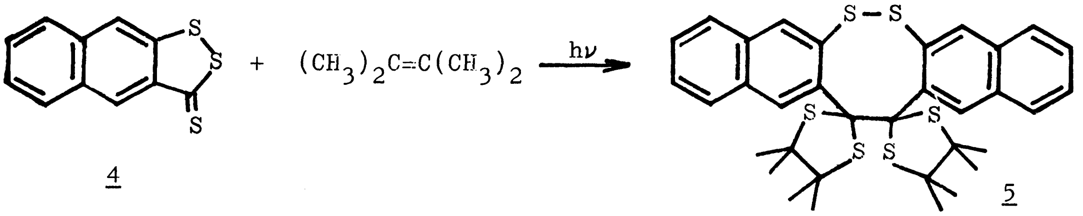
Reaction of o-thioquinone methide (1) ($R^1=R^2=CH_3$) with enamine (3) in acetonitrile—THF at 60 °C resulted in formation of colorless crystals (38%) with a molecular formula $(C_{13}H_{16}S_3)_2$ as evidenced by the elementary anylysis and molecular weight determination (vapor pressure osmometry in benzene; found: 568, Calcd 537). The NMR spectrum of this product consists of a slightly broad singlet



$$\underline{1}\ (R^1=R^2=CH_3)\ +\ CH_2=C\begin{matrix}\nearrow CH(CH_3)_2\\ \searrow N(CH_3)_2\end{matrix}\ \longrightarrow\ \text{Dimer B}\ (\underline{2}b)$$

3

of the methyl group (δ 1.52) and a multiplet of the aromatic protons (δ 7.0-8.3) in the ratio of 1:3, suggesting the structure of dimer B is not of [2+2] nor [4+2] type but of [4+4] type as in the case of dimer A.[5)] However, dimer B is clearly different from dimer A. The latter is colorless in the solid state but its dissolution in an appropriate solvent such as chloroform or THF leads to a deep blue solution due to dissociation into the highly colored monomer (1). On the contrary, dimer B remains colorless on dissolution or even on heating, although it gradually dissociates into 1 by light. The NMR spectrum of dimer A shows four singlets due to the methyl protons at δ 1.23, 1.33, 1.58, and 1.77 in contrast to a singlet in the case of dimer B. Supporting evidence that all the four peaks are due to the dimer, not, at least in part, to the monomer existing in solution as an equilibrium mixture was provided by the NMR spectrum of dimer (5)[6)] obtained by photoreaction of naphthodithiolethione (4)[7)] and 2,3-dimethyl-2-butene (Pyrex-filtered light from a high pressure mercury lamp, benzene, 20 min, 81%). The methyl region of the spectrum is very similar to that of dimer A, showing four singlets at δ 1.22, 1.46, 1.66, and 1.79.



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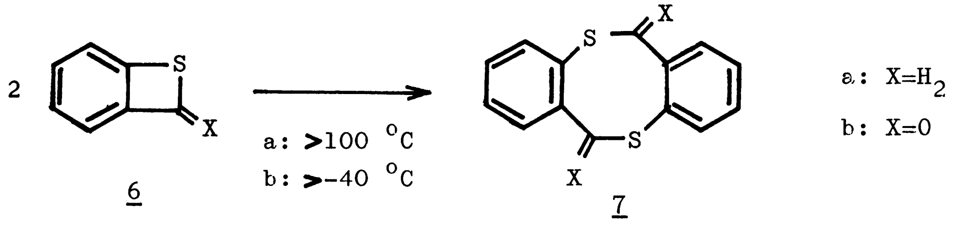
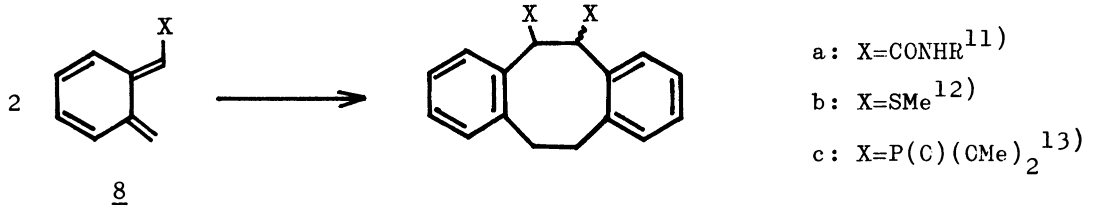
Inspection of the molecular model clearly indicates the following: 1) the eight-membered ring of the head-to-head [4+4] dimer (2a) is considerably distorted because of steric repulsion between the two dithiolane rings, thus making four pairs of methyl groups magnetically nonequivalent;[8)] 2) the head-to-tail dimer (2b) has an almost symmetrical structure with no such distortion, thus placing the methyl groups in nearly the same magnetic environment.[8)] On these bases, we conclude that dimer A is of head-to-head type and dimer B is of head-to-tail type. This is the first example of isolation of both head-to-head and head-to-tail dimers for o-quinonoid compounds.

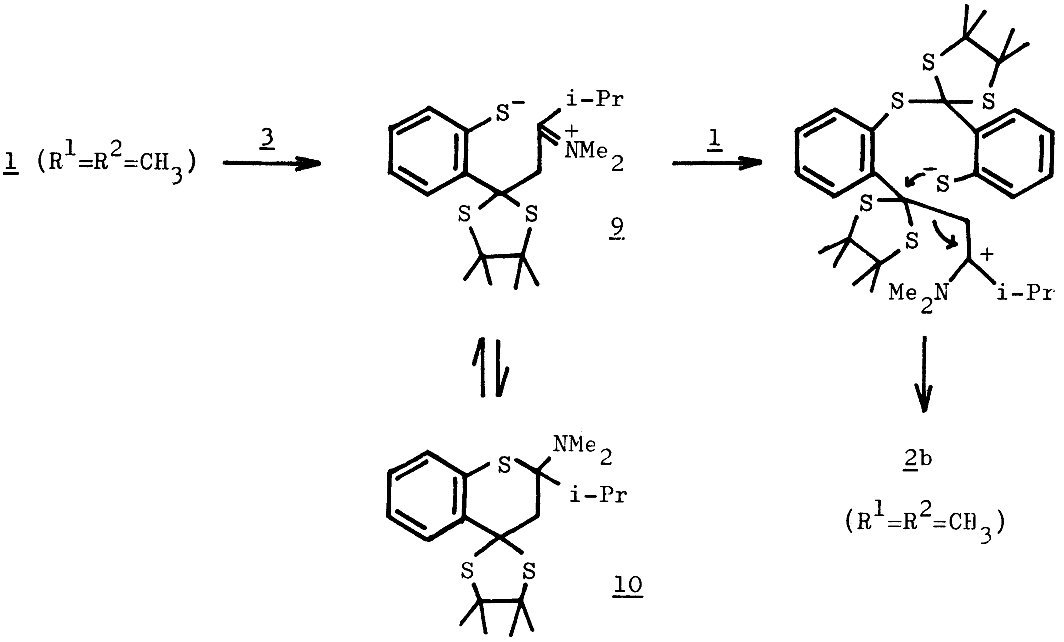
The fact that 1 dimerizes to afford the head-to-head dimer (2a) under normal conditions is noteworthy in view of a very recent report9) that the thermal dimerization of 6a results in dimer (7a), which most likely proceeds via the corresponding o-thioquinone methide. Benzothiolactone (6b) has also been reported to give rise to head-to-tail dimer (7b) upon dimerization.10)



Although we have no clear-cut explanation for this discrepancy, similarity of 1 to quinodimethanes (8a-c) in orientation of dimerization, which is most likely rationalized by a homolytic process involving diradical intermediates, seems to imply involvement of radical processes in our reaction as well.



The reaction mode observed in other enamine cycloadditions14) allows us to propose the following mechanism for the formation of dimer B. Equilibrium between 9 and 10 would be in favor of the former probably because of the presence of bulky isopropyl group in the case of this particular enamine, thus allowing the reaction with 1 to proceed further.15)



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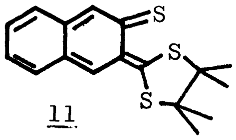
5) For a discussion of the structural determination, see Ref. 4).

6) We assigned the product to a head-to-head dimer 5 because it is highly unlikely that 11 exhibits a different regioselectivity in dimerization from 1. In contrast to the case of dimer A obtained from benzodithiolethione, no spectroscopic evidence for the existence of monomer 11 was obtained presumably because of intrinsic instability of such a conjugated system.16) The reaction solution (CH_2Cl_2) with tetramethylethylene irradiated at −78 °C did not show any color expected17) for 11, suggesting 11 is unstable even at such low temperatures to dimerize into 5.



11

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8) The fact that 2a and 2b bearing, in principle, eight and two kinds of different methyl groups show actually four and one methyl signals respectively suggests two methyl groups on the same carbon atom or on the same side of vicinal carbon atoms are magnetically nearly equivalent.

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17) o-Thioquinone methide (1) has very strong absorption ($\varepsilon > 7\times10^3$) at 585 nm.

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