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REDUCTION AS A PROBE FOR BENZOTHIIRENE INTERMEDIATES: THERMAL AND PHOTOCHEMICAL DECOMPOSITION OF 1,2,3 -BENZOTHIADIAZOLES.

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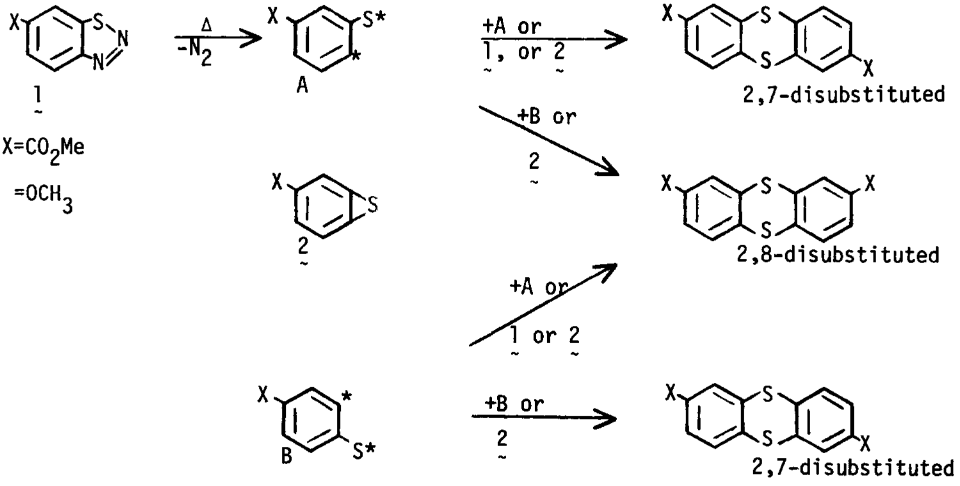
Abstract: Four benzothiadiazoles were either heated at reflux or irradiated at room temperature in tetrahydronaphthalene. The base soluble thiols which were obtained were converted to thiolacetates and analyzed by use of infrared and nmr shift-reagent spectroscopy.

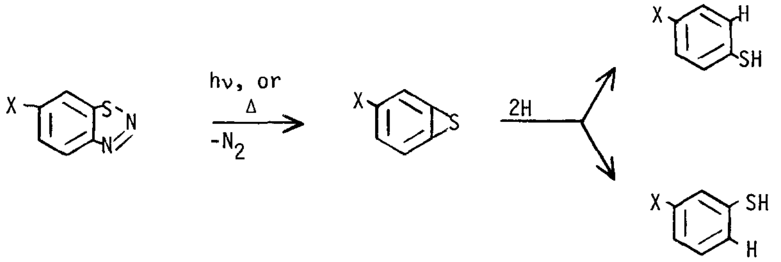
Benzothiirene as a highly reactive structure is of current interest. For example, loss of sodium bromide from sodium 4-methyl-2-bromobenzenethiolate to give 2,7- and 2,8-dimethylthianthrene may proceed through 3-methylbenzothiirene[1]. Further, heating 6-carbomethoxy-1,2,3-benzothiadiazole yields nitrogen and both 2,7- and 2,8-dicarbomethoxythianthrene[2]. 3-Carbomethoxybenzothiirene may be formed. (See Scheme I.) Low temperature irradiation of benzothiadiazole in an argon matrix yields 1,3-butadienylenethioketene and some other product whose infrared spectrum was assigned to benzothiirene[3]. Thermolysis of 6-methoxybenzothiadiazole apparently yields only 2,7-dimethoxythianthrene[4], a fact used to suggest that 3-methoxybenzothiirene did not form. Yet Scheme I shows two pathways from 6-methoxybenzothiadiazole to 2,7-dimethoxythianthrene.



Scheme I

Note that 2,8-disubstituted thianthrene forms only when intermediates with the stereochemistry of A and B combine[5]. If either A or B are largely predominant, a 2,7-thianthrene will be the major (and possible only detected) product .

In order to gain further information about possible intermediates involved in decomposition of benzothiadiazoles, thermal and photochemical extrusion of nitrogen in tetrahydronaphthalene, an H-donor solvent, was studied[6]. An anticipated, thiophenols formed (Equation 1).



(1)

X = OCH_3, Cl, CO_2CH_3, CH_3

Thus, each thiadiazole was either irradiated at room temperature through pyrex (4-8 hrs.) or heated at reflux (2-4 days) until nitrogen evolution ceased. The resulting thiols were removed from the reaction mixture by base extraction and converted to thiolacetates (acetyl chloride, pyridine). Analysis by use of infrared[7] and nmr-shift reagent[8] spectroscopy gave the results shown in Table 1.

Table 1: Yields of Thiols

6-Substituted Benzothiadiazole	Experiment Type	Total Yield	% para	% meta
methoxy	Δ	30	0	100
	hν	10	0	100
methyl	Δ	24	0	100
	hν	16	17	83
chloro	Δ	40	0	100
	hν	12	23	77
carbomethoxy[9]	Δ	53	7	93
	hν	36	31	69

Since the thiophenols involved in these experiments do not isomerize under these conditions[10], some structure such as a substituted benzothiirene is suggested. (See Equation 1). At this point clear conclusions about the nature of the intermediates (diradicaloid or carbenic) leading to the benzothiirene, whether an intermediate or a benzothiirene forms first, and which are reduced is not possible. However, the stereochemistry of the products requires the sulfur atom to become symmetrical at some point with respect to the aryl ring. The most reasonable structure for this segment of the molecule is benzothiirene. As is evident, benzothiirene forms in higher amounts at lower temperatures by irradiation. This result suggests, as apparently confirmed in studies of the parent system, benzothiadiazole[3], that benzothiirenes might be isolable at lower temperatures. Some work is in progress.

In refluxing tetrahydronaphthalene only intermediate A is important, except in the case when carbomethoxy is the substituent. For the irradiation experiments, intermediate B apparently forms except for the case where methoxy is the substituent. Since there are three intermediates involved, A,B, and thiirene **2**, it is impossible to comment as to whether a given substituent stabilizes or de-stabilizes a particular intermediate. (For example, consider the case where methoxy is the substituent and apparently only intermediate A forms. Methoxy either stabilizes A to such an extent that ring closure to thiirene **2** does not occur, or de-stabilizes A so that reduction by the environment is faster than ring closure.)

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(3) M. Torres, A. Clement, J.E. Bertie, H.E. Gunning, and O.P. Strausz, J. Org. Chem., **43**, 2490 (1978).

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(5) This scheme is not put forth as a mechanism. For example, no information has been obtained for the exact structure of A or B. The point to be stressed involves the necessary stereochemistry of the reacting intermediates.

(6) Decomposition of benzothiadiazole followed by reduction has been reported: H. Meier and H. Buhl, J. Heterocycl. Chem., **12**, 605 (1975). Products other than thiophenols produced in this work should have the same skeletal structures as those reported earlier by Meier and Buhl, and were thus not examined.

(7) With the exception of the carbomethoxy derivatives the infrared spectra of authentic samples of para- and meta-substituted thiolacetates contain strong adsorptions near 820 and 770 cm^{-1}, respectively, which were used to confirm the presence or absence of a particular isomer. For the carbomethoxy derivatives these peaks are shifted to near 775 and 750 cm^{-1}.

(8) The nmr spectra of mixtures of authentic samples of para- and meta-substituted thiolacetates and $Eu(fod)_3$ contain a singlet for the methyl group of the acetate of the para isomer downfield of the corresponding singlet of the meta isomer. (When shift reagent is added to mixture of the carbomethoxythiolacetates the methyl singlet of the carbomethoxy group separates before the methyl singlet of the thiolacetate, and was thus conveniently used for analysis. Again spectra of authentic samples show that the para-isomer singlet is downfield of that of the meta-isomer.)

(9) Extraction of the reaction mixture from 6-carbomethoxybenzothiadiazole gave the correspon ing thiolacid, which was reesterfied (acetyl chloride, methanol) before acetylation.

(10) Each of the following substituted thiophenols were subjected to the condition of the reaction. The starting thiol was recovered in each case uncontaminated with any other isomer: Substituent = p- and m-methoxy, p- and m-chloro, p- and m-carbomethoxy, and p- and m-methyl.

(11) N.S.F. Undergraduate Research Participant, 1978.

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