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THIABENZENES X. POSSIBLE ROLES FOR SULFURANE INTERMEDIATES IN "OLIGOMER" FORMATION

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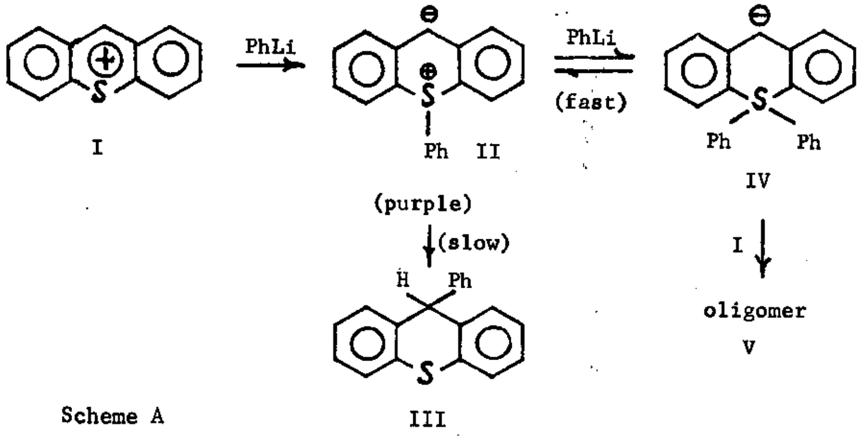
We fully confirm the already convincing evidence presented by Mislow et al. that materials we once identified as "stable thiabenzenes" are oligomers (of unknown structure). We present some experimental observations related to the hypothesis that these oligomers may have formed from reaction of a thiabenzene with phenyllithium through sulfurane-type intermediates.

Maryanoff, Stackhouse, Senkler and Mislow[1] have presented convincing evidence that the stable brown, amorphous materials we[2] had prepared by reaction of several thiopyrylium salts with phenyllithium are oligomers of unknown structure. We wish to report data here fully confirming their already convincing evidence, but also some experiments designed to test the hypothesis that the oligomers may have been formed from reactive thiabenzenes by further reaction with phenyllithium to give a sulfurane-like anion.

The hypothesis is illustrated for thioxanthylium ion as follows:



Scheme A

10-Phenylthioxanthenium perchlorate [1] suspended in ether was treated with phenyllithium in ether.[3] A wine red solution was formed. At -12°, the color persisted for nearly 30 min; but at room temperature had faded in 5 min. The ether solution was washed and analyzed by gas chromatography. The results are summarized in Table I.

Table I. Reaction of 10-Phenylthioxanthenium Perchlorate with Phenyllithium in Ether

Equivalent of PhLi	Temperature	% 9-Phenylthioxanthene
4	-12°	42
1	25°	80
3	25°	98

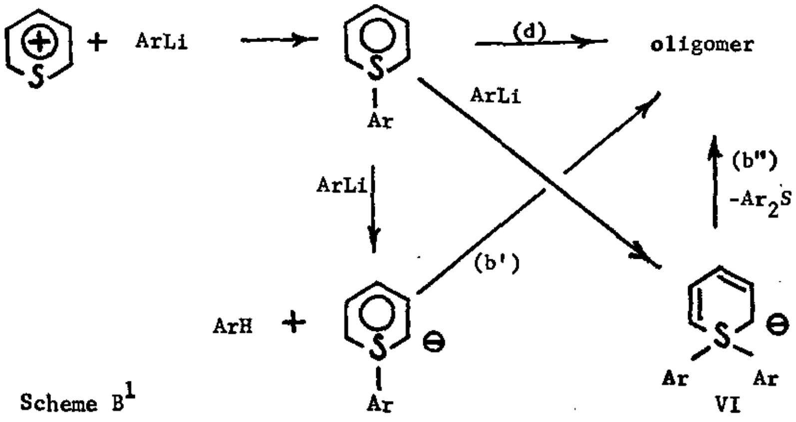
Oligomers were prepared by procedures described elsewhere.[1,2] Reaction mixtures were separated by fractional precipitation and mixtures were analyzed by gas chromatography.

From thioxanthylium perchlorate: Thioxanthene (12.1%), thioxanthenone (11.4%), 9-phenylthioxanthene (12.7%), bis-thioxanthenyl (mp 323-324°, 5.5%), oligomer (brown powder, sp 130-140°, molecular weight 431,[4] (11.8%).

Anal. Calcd for $C_{19}H_{14}S$: C, 83.27; H, 5.14; S, 11.58. Found: C, 83.27; H, 5.08; S, 11.33.

From 9-Phenylthioxanthylium perchlorate: 9-phenylthioxanthene (20.4%), 9,9-diphenylthioxanthene (7.4%), oligomer (brown powder, sp 139-143°, molecular weight 841, 31%).

Mislow et al.[1] and we now agree that the stable, brown amorphous materials we had earlier reported to be "stable thiabenzenes" are oligomers. They did some speculating about possible modes of formation based on the isolation of toluene and ditolyl sulfide from treatment of thiopyrylium (or thianaphthalinium) ion with tolyllithium. Mislow [1] suggested three possible routes for formation of oligomers.



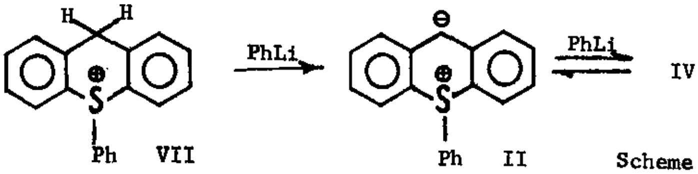
Scheme B[1]

These suggestions were tentative but do fail to explain two experimental facts satisfactorily; (1) that stable, brown amorphous oligomer is formed as well from 9-phenylxanthylium ion and phenyllithium as from other less substituted pyrylium salts (which eliminates route b') and (2) that the oligomers usually give elementary analyses very satisfactory for the thiabenzene structure (which eliminates route b").

Since 9-phenylthioxanthylium ion and the 9,10-diphenyl-10-thiaanthracene related to it have no hydrogens on the hetero ring, hydrogen abstraction seems an unsatisfactory hypothesis in this case. Also, the purple thianaphthalenes made by D. H. Follweiler[5] from 1-phenyl- and 1-*t*-butyl-2-thionaphthalenium ion and phenyllithium were *not* accompanied by brown oligomer despite having potentially reactive α- and β-hydrogens on the hetero ring. Rather, these two thiabenzenes were ready acceptors of a proton to give 2-thiochromenium salts.[4]

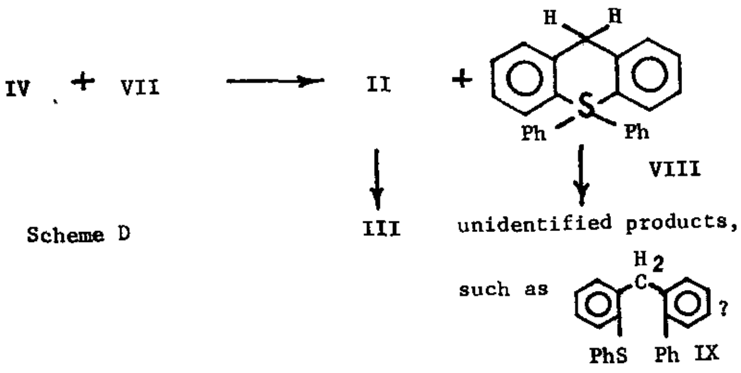
Formulation of thiabenzenes as zwitterionic ylids [1,6] does, of course, present the possibility of direct conversion of thiabenzenes to oligomers (Scheme B, (d)). The fact that formation of thiabenzenes by deprotonation (Scheme C) does *not* produce oligomer is a strong argument against this route.

We are therefore led to suggest that oligomer is formed from the sulfurane anion by reaction with the starting thiopyrylium cation (Scheme A). We decided to test this hypothesis by the following sequence of reactions.



Scheme C

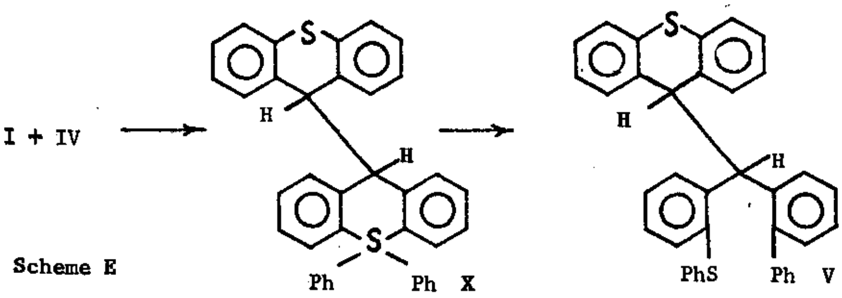
In our experiments, we were unable to identify IV (or clean-cut products from IV) but we nevertheless do suggest our observations support this scheme. The main isolated product from the reaction of VII with phenyllithium was III, the rearrangement product of II. However, the yield of III was influenced by the reaction temperature and the excess of phenyllithium used, increasing to nearly 100% of III from VII when a large excess of phenyllithium was employed and decreasing at low temperatures. These observations would fit with Scheme C if IV could react with VII to give unidentified by-products. The larger the excess of phenyllithium, the less VII would be present to react with IV. The lower the temperature the slower would VII be converted to II. At -12°, only 42% of III was recovered, which would fit with the following scheme.



Scheme D

The isolation of ditolyl sulfide [1] from tolyllithium and thiopyrylium (or thianaphthalenium) ion is satisfactorily explained by the intermediate sulfurane VI decomposing to eliminate diaryl sulfide. The resulting hydrocarbon anion could be cyclopentienylide anion from thiopyrylium ion or indenylide anion from naphthalenium ion. Each of these anions could very readily be converted to a hydrocarbon polymer. An analogous reaction for IV would, however, produce fluorenylide anion, very unlikely to produce a polymer. We therefore suggest that oligomer is formed by the alternate mode of cleavage to give the diaryl sulfide IX.

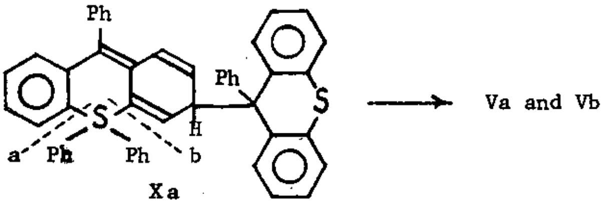
The analogous reaction of I with IV could presumably not produce VIII. One possibility is an oligomeric ion pair, the second, an unstable covalent compound X which would react further to give the stable brown oligomer. A ring opening reaction analogous to VIII producing IX would suggest one possible structure for the oligomer as indicated in Scheme E (V).



Scheme E

For oligomer from both thioxanthylium and 9-phenylthioxanthyliun ion, the molecular weights of oligomer are close to the values expected for dimer. For thionaphthalenium ion, the molecular weights observed here and at Princeton are significantly greater than dimer. In this case, however, the product corresponding to V (Scheme E) would have a vinylic double bond in a thiopyran type ring, known to be readily susceptible to polymerization.

An alternate course for anion-cation coupling, especially starting with 9-phenylthioxanthylium ion, is illustrated by structure Xa below.



Xa

The hexadiene ring might be the source of further oligomerization. Ring opening at the sulfurane could now occur to give isomeric structures. This and a hydride shift to rearomatize the diene ring would give a number of isomeric stable aromatic compounds (Va and Vb) which might help explain the amorphous nature of the "oligomer".

When the amorphous oligomer from 9-phenylxanthylium ion and phenyllithium (V) was oxidized by hydrogen peroxide in acetone, it gave 69% of an orange-brown solid giving elementary analyses in excellent agreement for the bis-sulfoxide of V, Va and Vb. The strongest band in the infrared (1200 cm^{-1}) also indicated a sulfoxide structure.

From the doctoral dissertation of Joanne Follweiler, University of Pennsylvania, Philadelphia, Pennsylvania 19104 (1977).

1 See, e.g. B. E. Maryanoff, J. Stackhouse, G. H. Senkler, Jr. and K. Mislow, *J. Am. Chem. Soc.*, 1975, **97**, 2718.

2 (a) C. C. Price, M. Hori, T. Parasaran and M. Polk, *J. Am. Chem. Soc.*, 1963, **85**, 2278; (b) M. Polk, M. Siskin and C. C. Price, *J. Am. Chem. Soc.*, 1969, **91**, 1206.

3 J. Evans and C. Allen, J. Org. Syn., Coll. Vol. II, John Wiley & Sons, Inc., N. Y., N. Y., 1943, p. 518.

4 By Hitachi Perkin Elmer Molecular Weight Apparatus, Thermistor Type. By gel permeation, the molecular weight maximum was at 500 a.m.u.

5 C. C. Price and D. H. Follweiler, *J. Org. Chem.*, 1969, **34**, 3202.

6 It is somewhat amusing that we were misled by misinterpreting the oligomers as "stable thiabenzenes" into suggesting covalent structures, rather than ylid structures for thiabenzenes. In our book on "Sulfur Bonding" (with S. Oae, Ronald Press, N. Y., 1962) we had presented convincing (although frequently ignored) arguments that representation of the sulfur oxygen bond in sulfoxides and the like as a covalent double bond is logically incorrect. While such properties as bond length, bond strength and bond polarity are equally well represented by either the covalent or the zwitterionic structure, lack of covalent addition reactions and, more important lack of bond polarizability (as measured by molecular refraction, parachor, etc.) are *totally* inconsistent with the covalent double bond structure.

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