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THIABENZENES. XI. THE REACTION BETWEEN THIOXANTHYLIUM AND PHENYLMERCAPTIDE IONS

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The main products of the titled reaction are thioxanthenone and thioxanthene. By chromatography, a small amount (0.5—1.5%) of a purple solid was obtained which had properties consistent with those expected for 10-phenylthio-10-thiaanthracene.

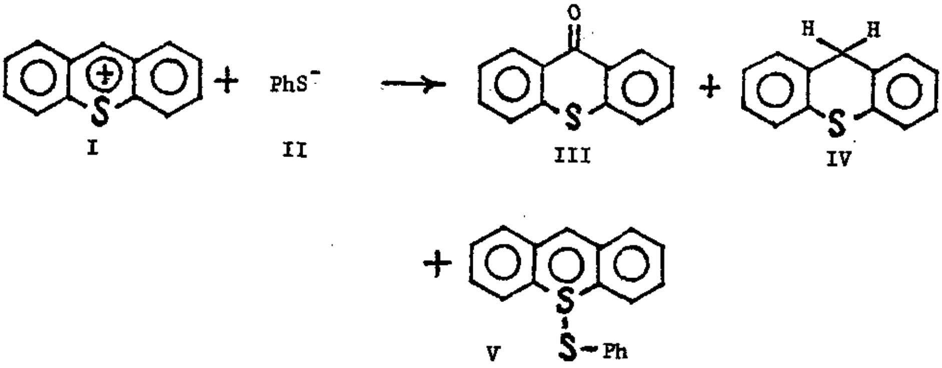
Several thiopyrylium salts couple with phenyllithium to give purple thiabenzene derivatives [1,2,3] while other thiopyrylium salts give amorphous oligomers, perhaps through thiabenzene intermediates.[4,5]

It seemed of interest to explore the reaction of a thiopyrylium ion with an anion, other than a carbanion, which might possibly couple to form a stable bond to sulfur. For this purpose we have studied the reaction of thioxanthylium perchlorate with lithium and potassium phenylmercaptide.

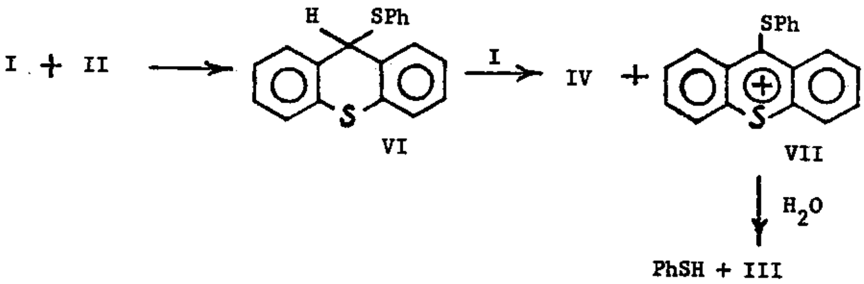
The latter salt, prepared in ether from phenylmercaptan and one equivalent of potassium t-butoxide, was allowed to react with thioxanthylium perchlorate in ether under nitrogen. The orange reaction mixture, containing some white precipitate was separated by precipitation and liquid followed by gas chromatography . Two main fractions were thioxanthenone (III, 57%) and thioxanthene (IV, 45%). A small amount (0.6%) of purple solid (V) was isolated.

When lithium phenylmercaptide, generated by treating phenyllithium with excess sulfur, was used, the yields were 57% III, 29% IV and 1.6% V.

The purple solid, sp $59-75^{\circ}$, showed λ_{max} (EtOH) at 500 nm (log ϵ 2.52) when fresh, shifting to λ_{max} 460 nm, log ϵ 1.47 on standing. A mass spectrum showed peaks at amu 197 (100%), 212 (94), 184 (37), 218 (29) and 109 (28), assigned to thioxanthylium, thioxanthenone, dibenzothiophene, diphenyl disulfide and phenylmercaptide ions, respectively. There was no peak corresponding to amu 306 (parent) but a weak peak was present at 294 (4%). Presumably the diphenyl disulfide and thioxanthenone were present as impurities. Fragment ions which support the structure V were thioxanthylium (197 amu, 100%), phenylmercaptide (109 amu, 28%), phenyldisulfide (141 amu, 5%) and $C_{13}H_9$ (165 amu, 16%, fluorenyl?).



The failure to detect any bithioxanthyl in the reaction mixture is an argument against one-electron exchange reactions and free radical intermediates for the reaction of I and II. We suggest that the formation of III and IV can be explained readily by the following sequence of reactions. In view of the rapid rearrangement of 10-phenyl-10-thiaanthracene to 9-phenylthioxanthene,[4] VI might be formed by sulfur-to-sulfur coupling followed by rapid rearrangement, as well as by direct coupling at the 9-carbon.



Hydranion exchange between VI and I to give IV and VII should be favored by the enhanced stability of the 9-carbocation in VII by means of electron donation from the sulfur at the 9-position.

There was insufficient sample of purple solid for elementary analysis. The suggested assignment of structure V is tentative, although the absorbance at 500 nm,[4] the instability on storage, the solubility and softening behavior and the fragementation patterns in the mass spectrum are as expected for V.

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