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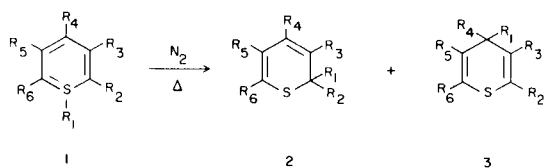
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The rates of rearrangement in 1-phenyl-2,4,6-tris(*p*-methoxyphenyl)thiabenzene (**4**) and 1-(*p*-trifluoromethylphenyl)-2,4,6-triphenylthiabenzene (**5**) were determined and a crossover experiment was carried out with a mixture of these thiabenzenes. The possibility of 2,4-migrations in the thiopyran system under the reaction conditions was also studied by examining two samples of thiopyrans. The results indicate an intramolecular rearrangement which involves a 1,2- and 1,4-migration of *S*-aryl groups in thiabenzenes.

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The thermal rearrangement of thiabenzenes (**1**) to their isomeric 2- and 4-thiopyrans (**2** and **3**) has been reported for a number of *S*-alkyl and *S*-aryl derivatives, with the 4-isomer (**3**) being the major product. There are significant differences between the rates of this rearrangement in different thiabenzenes. The chemical and spectroscopic data (2,3) reveal that 1-alkyl-2,4,6-triarylthiabenzene (**1a**) rearrange much more rapidly than 1,2,4,6-tetraarylthiabenzene (**1b**). While electron donating groups attached to the 1-aryl ring decrease the rate of rearrangement, electron donating groups on the 2,4,6-aryls increase the rate (4). By contrast, the effect of electron withdrawing groups on the ease of rearrangement is opposite to the effect of electron donating groups (5). In addition to the electronic effects, replacement of the 3- and 5-hydrogen atoms of the sulfur ring in 1,2,4,6-tetraarylthiabenzene with a bulky group such as methyl (**1c**) also increases the rate of rearrangement (3). Although many reports are available on thiabenzene rearrangements, the experimental data on mechanism are limited (3,6). In order to elucidate the mechanism, we now wish to report here on the kinetics and the crossover experiment with two thiabenzene derivatives which appeared to be suitable for this investigation, together with the evidence we have observed in the thiopyran system.



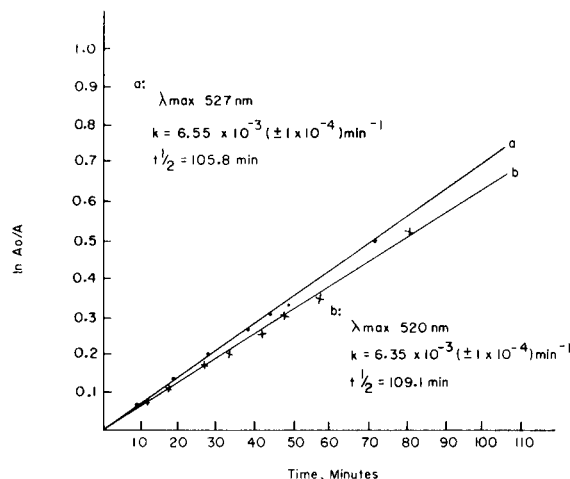
**a**,  $R_1$  = alkyl;  $R_2 = R_4 = R_6$  Phenyl;  $R_3 = R_5 = H$

**b**,  $R_1, R_2, R_4, R_6$  = aryl;  $R_3 = R_5 = H$

**c**,  $R_1$  = Phenyl, *p*-tolyl;  $R_2 = R_4 = R_6$  = Phenyl;  $R_3 = R_5$  = methyl

In the course of our study on thiabenzenes, we had noted that 1-phenyl-2,4,6-tris(*p*-methoxyphenyl)thiabenzene (**4**) and 1-(*p*-trifluoromethylphenyl)-2,4,6-triphenylthiabenzene (**5**) rearrange slowly to the cor-

responding thiopyrans (**6,7** and **8**) at about the same rates. To study the kinetic order of thiabenzene rearrangement and put the relative rates on a quantitative basis, the ethereal solutions of thiabenzene **4** and **5** were prepared under dry nitrogen in three different concentrations at  $-60^\circ$  and retained in the dark at room temperature. The characteristic thiabenzene absorptions ( $A$ ) of the purple solutions were measured near 500 nm at periodic time intervals, and the values were plotted in terms of  $\ln A_0/A$  versus time. Then the rate constants ( $k$ ) and the half-lives ( $t_{1/2}$ ) were determined for each compound in different concentrations. Considering the unavoidable errors involved in the rate constant measurements of the oxygen-sensitive compounds **4** and **5**, the values for the three different runs for each compound were in good agreement. The average rate constants obtained were  $6.55 \times 10^{-3} (\pm 1 \times 10^{-4}) \text{ min}^{-1}$  ( $t_{1/2} = 105.8$  minutes) for **4**, and  $6.35 \times 10^{-3} (\pm 1 \times 10^{-4}) \text{ min}^{-1}$  ( $t_{1/2} = 109.1$  minutes) for **5** at  $22 \pm 2^\circ$ . The kinetic results, which are in agreement with first-order reactions, are shown in the following figure.



The plots of  $\ln A_0/A$  versus time for **4** (a) and **5** (b) in ether solution at  $22 \pm 2^\circ\text{C}$  representing the first-order reactions.

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Since the half-lives appeared to be about the same for both thiabenzenes, it was decided to carry out a crossover experiment using **4** and **5**. Ethereal solutions of **4** and **5** were separately prepared under dry nitrogen and mixed after quenching with a saturated aqueous solution of ammonium chloride. The purple mixture was retained under nitrogen until the color of the solution turned orange. The oily residue was subjected to thin layer chromatography and mass spectrometric analysis, where the crude reaction mixtures of **4** and **5** were used as references. 4-Phenyl-2,4,6-tris(*p*-methoxyphenyl)thiopyran (**6**), 2-phenyl-2,4,6-tris(*p*-methoxyphenyl)thiopyran (**7**) and 4-(*p*-trifluoromethylphenyl)-2,4,6-triphenylthiopyran (**8**) were the only compounds that could be detected in the mixture of rearrangement products. There were no new spots in the tlc or any additional peaks in the mass spectrum at *m/e* 560 and 402 that could be attributed to the crossed products 4-(*p*-trifluoromethylphenyl)-2,4,6-tris(*p*-methoxyphenyl)thiopyran (**9**) and 2,4,4,6-tetraphenylthiopyran (**10**). It should be mentioned that the 4-crossed products **9** (**5**) and **10** (**2**) are known compounds, whereas the crossed 2-isomers, 2-(*p*-trifluoromethylphenyl)-2,4,6-tris(*p*-methoxyphenyl)thiopyran and 2,2,4,6-tetraphenylthiopyran, have not yet been characterized.

It is therefore concluded that the rearrangement of the *S*-aryl thiabenzenes is an intramolecular rearrangement which may proceed according to the following three pathways: (a) Separate 1,2- and 1,4-intramolecular rearrangements; (b) A sequence of 1,2- and 2,4-intramolecular rearrangements with no direct 1,4-migration; (c) A combination of paths a and b. To test the possibility of 2,4-rearrangement in the thiopyran system, a pure sample of 2-methyl-2,4,6-triphenylthiopyran (**2a**,  $R_1 = \text{methyl}$ ) was allowed to stand in ethereal solution under nitrogen for several days. The solution was then tested by uv and nmr. No evidence indicating the formation of 4-methyl-2,4,6-triphenylthiopyran (**3a**,  $R_1 = \text{methyl}$ ) was observed. Moreover, an ethereal mixture of thiopyrans **6** and **7** was examined in the same way, and no increase in the amount of the 4-isomer (**6**) could be detected. Thus, the possibility of the 2,4-rearrangement in the thiopyran system under

the reaction conditions, as well as the possibility of pathways b and c in the thiabenzene rearrangement were excluded.

The experimental data reported here reveal that the rearrangement of *S*-aryl thiabenzenes to their isomeric thiopyrans is substantially an intramolecular rearrangement which involves a 1,2- or 1,4-migration of *S*-aryl groups. These results are in support of the earlier reports which describe thiabenzene migrations as Stevens-type rearrangements (3,6).

## EXPERIMENTAL

Ultraviolet and visible absorption spectra were recorded on a Varian Techtron uv-visible spectrophotometer Model 635. Nmr spectra were determined on a Varian T-60 spectrometer. Mass spectra were measured on a Varian Model CH-5 spectrometer.

The Kinetic Study of 1-Phenyl-2,4,6-tris(*p*-methoxyphenyl)thiabenzene (**4**).

The procedure reported earlier for the synthesis of **4** (**4**) was modified in this study. In a 5 ml. cuvette equipped with rubber septum cap and flushed with dry nitrogen were placed about  $2 \times 10^{-4}$  mmole of 2,4,6-tris(*p*-methoxyphenyl)thiopyrylium perchlorate and a few ml. of oxygen-free dry ether. The mixture was allowed to stand under nitrogen atmosphere at  $-60^\circ$  for 20 minutes. One equivalent of 0.8*M* ethereal phenyllithium was then added through the septum cap, and the mixture was stored in the dark at  $22 \pm 2^\circ$ . At periodic time intervals, the absorbances (*A*) of the resulting purple solution were recorded at 527 nm. This experiment was repeated for two other concentrations of the perchlorate. The  $\ln A$  values were plotted *versus* time and the value of  $A_0$  for each sample was determined by extrapolation of the resulting straight lines to zero time. The values of the rate constants (*k*) and half-lives ( $t_{1/2}$ ) were calculated from the linear plots of  $\ln A/A_0$  *versus* time. The rate constants were almost the same for all samples. The average value obtained was  $k = 6.55 \times 10^{-3} (\pm 1 \times 10^{-4}) \text{ min}^{-1}$  with  $t_{1/2} = 105.8$  minutes.

The Kinetic Study of 1-(*p*-Trifluoromethylphenyl)-2,4,6-triphenylthiabenzene (**5**).

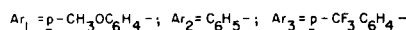
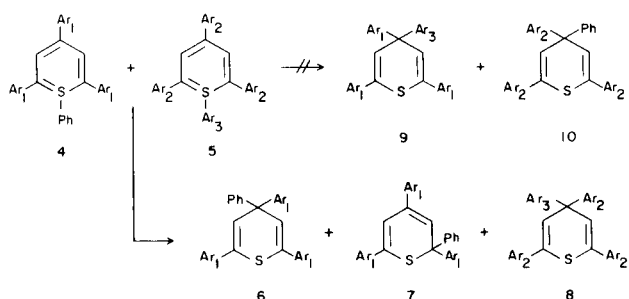
Following the above procedure with the corresponding thiopyrylium perchlorate (**5**), the absorbances (*A*) were recorded at 520 nm, and the plots of  $\ln A/A_0$  *versus* time were drawn for different samples of **5**. The rate constants calculated from the resulting lines were essentially the same for all the samples. The average value obtained was  $k = 6.35 \times 10^{-3} (\pm 1 \times 10^{-4}) \text{ min}^{-1}$  with  $t_{1/2} = 109.1$  minutes.

The Crossover Experiment With **4** and **5**.

Ethereal solutions of thiabenzenes **4** and **5** were separately prepared from 10 mmoles of the corresponding thiopyrylium perchlorates (**4,5**) and mixed ten minutes after quenching with ammonium chloride solution. The dried organic layer of the mixture was left to stand overnight under a nitrogen atmosphere. An aliquot of the orange solution was evaporated and the oily residue subjected to tlc on alumina with ether-petroleum ether (40:60) as eluent. No new spots were observed for the crossed products **9** and **10** as determined by the crude reaction mixtures of **4** and **5** prepared separately. A comparison of the mass spectra of these crude mixtures with that of the crude oily residue of this experiment showed no additional peaks at *m/e* 560 and 402 that could be attributed to the crossed products **9** and **10**.

Thiopyran Studies.

A sample of 2-methyl-2,4,6-triphenylthiopyran (**2a**,  $R_1 = \text{methyl}$ ) (**2**) was dissolved in ether and allowed to stand under nitrogen on exposure to daylight for nine days. Then, the uv and nmr spectra of the solution were recorded. No changes in spectra could be observed at the end of this time.



In another experiment an ethereal solution of a mixture of **6** and **7** (4) was examined under the above conditions. Although the uv and nmr spectra of this solution had greatly changed, there was no increase in the amount of **6**.

Acknowledgment.

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