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## Phosphorus, Sulfur, and Silicon and the Related Elements

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## 1,3-THIAZOLIDINIC AND 2,4,5,6-TETRAHYDRO-1,3-THIAZINIC SPIROCHROMENES AND MEROCYANINES. SYNTHESIS, REACTIVITY AND PHOTOCHROMIC PROPERTIES

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1,3-THIAZOLIDINIC AND 2,4,5,6-TETRAHYDRO-1,3-THIAZINIC SPIROCHROMENES AND MEROCYANINES. SYNTHESIS, REACTIVITY AND PHOTOCHROMIC PROPERTIES.

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The synthesis of spirochromenes (I and II) and merocyanines (I' and II') in 1,3-thiazolidinic and 1,3-thiazinic series, is carried by

condensation, in basic medium, of salicylic aldehyd on heterocyclo-ammonium salts issued from  $\Delta 2$ -thiazolines (III) and 5,6-dihydro-4H -1,3-thiazines (IV) bases, having the following general structure:

$$\begin{array}{c|c}
R_{i}^{"}C \\
R_{i} \\
R_{4} \\
R_{4}
\end{array}$$

$$\begin{array}{c|c}
CH_{2}R_{3} \\
R_{4} \\
R_{4}
\end{array}$$

$$\begin{array}{c|c}
n = 1 & [III] \\
n = 2 & [IV]$$

In the course of preparation of these bases some interesting results have been summarized. The synthesis of  $\Delta 2$ -thiazolines from episulfides in acidic medium, may proceed by many ways because opening of episulfide is possible at the less substituted carbon atom. This process however being minor brings to the formation of isomer  $\Delta 2$ -thiazolines. We have checked too that sulphuration of 5,6-dihydro-4H-1,3-oxazines into 1,3-thiazines (IV), according to A.I. Meyers (1,2), is not a stereospecific reaction . The formation of by-products is observed during the preparation of spirochromenes and merocyanines and is related to the behavior of these compounds towards nucleophilic reagents such as water or hydrogen sulfide. Coumarins, substituted 1,3-thiazolidines or 2,4,5,6-tetrahydro-1,3-thiazines have been identified. Moreover spirochromenes and merocyanines are reactive towards sodium borohydride with opening of chromene cycle or partial reduction. Finally the photochromic equilibrium spiropyran photomerocyanine was studied by flash photolysis technique and the influence of electronic and steric effects of different substituents on spectrokinetic parameters have been stressed. Comparisons in the field of "colorability" and visible absorption of thiazolidinic and thiazinic photomerocyanines have been made.

- (1) A.I. Meyers, J.org.Chem., 1960, 25, 1147
- (2) A.I. Meyers, J.org.Chem., 1961, 25, 218