with water, giving α-stilbene dichloride (3.8 g., 9.6%), which on recrystallization from ethanol gave needles melting at 191–193° (literature m.p. 191–193°).[5] No depression of the m. p. was observed on admixture with the authentic material prepared from hydrobenzoin and phosphorus pentachloride.

trans-Stilbene (II) *from α-stilbene dichloride* (I). A mixture of α-stilbene dichloride (2.0 g.), iron powder (20 g.), and water (100 cc.) was refluxed for 24 hours. The reaction product was extracted with benzene. After evaporating the solvent, the crude material was recrystallized from alcohol, yielding 1.0 g. (70%) of *trans*-stilbene, m.p. 122–124° and mixture m.p. 122–124°.

Tolane tetrachloride (III) *from benzotrichloride.* To a mixture of water (50 cc.) and reduced iron powder (12.6 g., 0.225 mole) was added benzotrichloride (29.3 g., 0.15 mole) with vigorous agitation in a boiling water-bath and the reaction product was worked up as before. There was obtained 6 g. (25%) of tolane tetrachloride, which on recrystallization from acetic acid gave 4.8 g. of the pure material, m.p. 160–162° literature m.p. 163°,[6] 162°,[7] and 161.5°).[8]

Anal. Calc'd for $C_{14}H_{10}Cl_4$: C, 52.49; H, 3.12; Cl, 44.32. Found: C, 52.48; H, 3.25; Cl, 44.00.

trans-α,α'-dichlorostilbene (IV) *from tolane tetrachloride* (III). The work-up with tolane tetrachloride (0.5 g.) was the same as with stilbene from α-stilbene dichloride, except that the reaction was stopped after 4 hours. The α,α'-dichlorostilbene melted at 143–145° (literature m.p. 153°,[9] 150°,[8] 143°,[6] 142°,[10]) and gave no depression on admixture with an authentic sample; the yield was 0.25 g. (64%).

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(5) Zincke, *Ber.*, **10**, 996 (1877).

(6) Liebermann and Homeyer, *Ber.*, **12**, 1971 (1879); Blank, *Ann.*, **248**, 1 (1888).

(7) Onufrowicz, *Ber.*, **17**, 833 (1884).

(8) Marckwald and Karczag, *Ber.*, **40**, 2994 (1907).

(9) Zinin, *Ber.*, **4**, 289 (1871); Limpricht and Schwanert, *Ber.*, **4**, 379 (1871).

(10) Staudinger, *Ber.*, **49**, 1969 (1916).

Zolon Red and the Zolon Red-Silver Complex[1]

GEORGE F. SVATOS AND JEROME GOLDENSON

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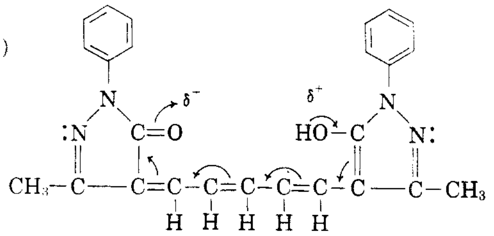
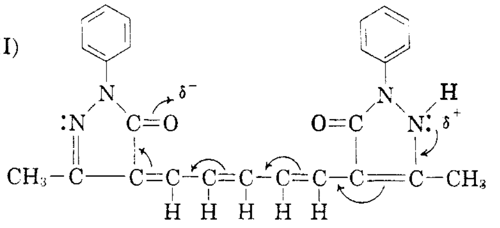
The monomethine oxonol derived from 1-phenyl-2-methyl-pyrazolone-5 was described by Knorr.[2] Later, dyes such as zolon blue, (I), which contain the $(\text{—CH=CH—})_n$ group were prepared and their chromophoric activity discussed.[3] While working with zolon blue Gehauf and Goldenson[1] found that treatment with an alkaline solution produced a red product, zolon red. This new dye was found to be a useful analytical reagent for silver. Though its analytical application was discussed in some detail, little was known about the constitution of zolon red and its silver complex; this is examined in the work of this report.

Zolon blue and zolon red have identical empirical formulas and therefore appear to be isomeric. Gaspar[3] indicated that more than one tautomeric form may exist for a given dye formula in this system. These variations are well known in 1-phenyl-3-methyl-pyrazolone-5.[4] The most likely tautomeric forms of the zolon blue–zolon red systems are as follows:

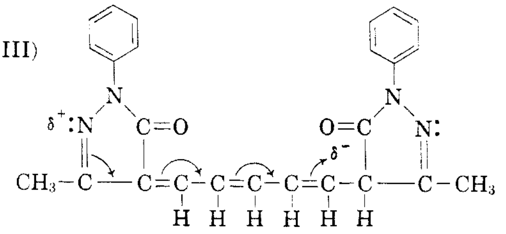
(I)



(II)



(III)



(I) and (II) have the longest conjugated chains and greatest π-electron mobility.

In the work reported here, corresponding differences were observed in the visible and infrared absorption spectra of these dyes. Zolon blue absorbs strongly at 620 millimicrons and zolon red at 522 millimicrons (Fig. 1). This hypsochromic shift occurs with decreasing chain length where a lower π-electron mobility exists.[5,6] In acid solution both compounds show a hypsochromic shift to 430 millimicrons. When neutralized with base these acidified solutions again show their characteristic 522 and 620 millimicron bands indicating that the

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(1) B. Gehauf and J. Goldenson, *Anal. Chem.*, **27**, 420 (1955).

(2) L. Knorr, *Ann.*, **238**, 184 (1887).

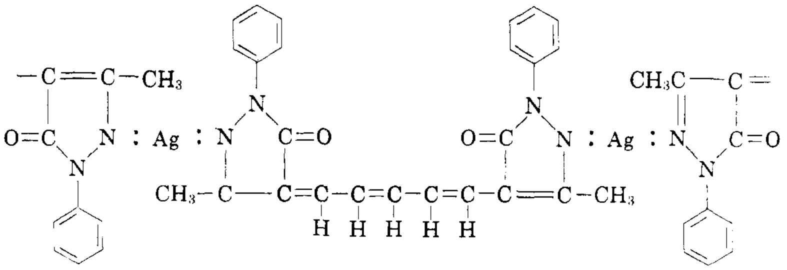
(3) B. Gaspar, U. S. Patent 2,274,782; *Chem. Abstr.*, **36**, 4042 (1942).

(4) P. Karrer, *Organic Chemistry*, Elsevier, New York, 1946, p. 773.

(5) G. W. Wheland, *The Theory of Resonance*, Wiley, New York, 1944, pp. 157–158.

(6) R. E. Burk and O. Grummitt, *Advances in Nuclear and Theoretical Organic Chemistry*, Chap. IV by L. G. S. Brooker, Interscience, New York, 1945, p. 99.

(IV)



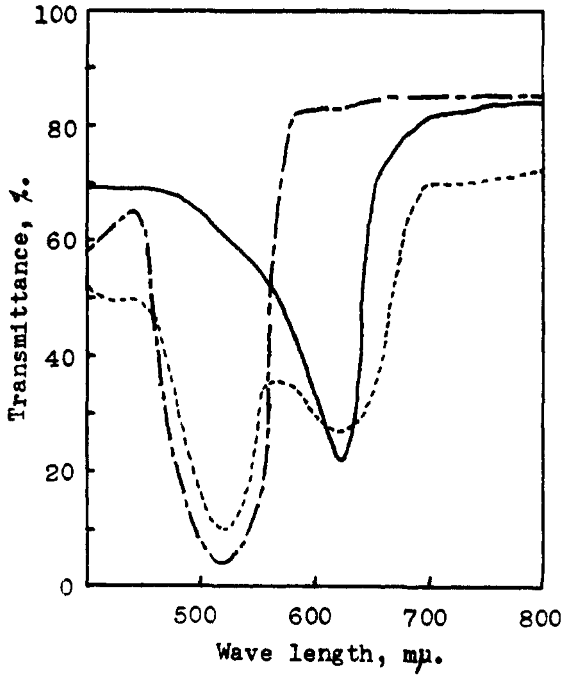


FIG. 1.—Comparison of spectra of zolon blue, ————; zolon red, — — — —; Ag(I) zolon red complex, --------.

parent compounds are left unchanged. No shift was observed in basic solutions of zolon red. Those of zolon blue indicated a chemical change took place.

The infrared spectra of compounds of this type are complex. The broader and more rounded absorption bands of zolon blue indicate that its resonance transitions are more variable than those of zolon red. The red dye shows a single, strong, sharp carbonyl absorption at 5.96 microns while the blue dye gives a broader, more complex absorption at 5.90 microns. In the O—H and N—H region zolon red shows no absorption: The blue dye gives a broad band. Structure (III) appears to agree most closely with the zolon red spectrum and (I) or (II) with that of zolon blue.

It was also found from a continuous variation study (Fig. 2) and chemical analysis that zolon red and the silver ion form a 1:1 coordination compound. Under similar conditions zolon blue gave a solid material of indefinite composition. The silver ion has s-p orbitals available for coordination which results in linear coordinate bond formation.[7] The availability and distribution of electron pairs on nitrogen atoms in zolon red makes a chain structure similar to (IV) probable. Resonance contributes to the strength of the coordinate bond.[8] The very low solubility of this complex is also in agreement with the proposed structure.

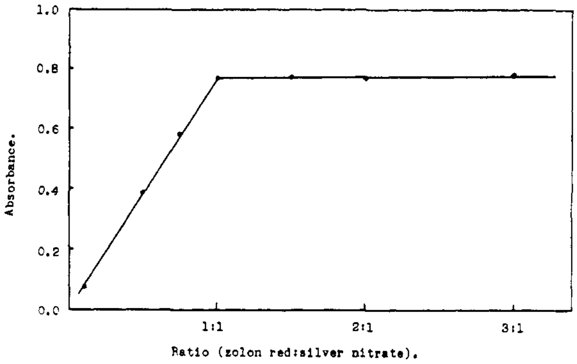


FIG. 2.—CONTINUOUS VARIATION STUDY.

Visible absorption spectra of the complex show two bands; one at 620 millimicrons and one at 522 millimicrons (Fig 1). Chromophoric activity similar to that in the zolon red and zolon blue system seems to be present in the complex. Examination of the carbonyl absorption region of the infrared spectrum shows a single, sharp band at 6.05 microns indicating only one species of carbonyl exists.

EXPERIMENTAL

Preparation of reagents. Zolon blue and zolon red were prepared according to the procedure outlined by Gehauf and Goldenson.[1] Both were recrystallized three times from absolute methanol and dried under a vacuum over phosphorus pentoxide at 110°.

Anal. Calc'd for zolon blue, $C_{25}H_{22}N_4O_2$: C, 73.15; H, 5.40; N, 13.65. Found: C, 72.40; H, 5.23; N, 14.14.

Anal. Calc'd for zolon red, $C_{25}H_{22}N_4O_2$: C, 73.15; H, 5.40; N, 13.65. Found: C, 72.50; H, 5.39; N, 14.40.

Preparation of the silver-zolon red complex. To a solution containing 0.2 g. (0.0005 mole) of zolon red dissolved in 200 ml. of methanol was added 0.085 g. (0.0005 mole) of silver nitrate dissolved in 50 ml. of water. A blue colloidal precipitate formed immediately. This mixture was heated to 50° and then allowed to cool in a dark cabinet. The supernatant solution was removed by means of a pipette and the precipitate was washed with water and allowed to settle. The complex was washed three times in this manner using water, absolute methanol, and ether. It was then filtered through a

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(7) L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, New York, 1945, p. 89.

(8) A. E. Martell and M. C. Calvin, *Chemistry of the Metal Chelate Compounds*, Prentice Hall, New York, 1952, p. 160.

fine sintered glass funnel. The precipitate was dried in the open air, powdered, and then dried in a vacuum over phosphorus pentoxide at 100° for ten hours. A yield of 99% was obtained.

Anal. Calc'd for $Ag(C_{25}H_{21}N_4O_2)$: C, 58.04; H, 4.09; N, 10.83. Found: C, 57.50; H, 4.20; N, 10.70.

Visible spectra. Visible spectral data were obtained using the Cary automatic recording spectrophotometer and the Beckman Model DU spectrophotometer with 1-cm. quartz cells. Stock solutions of zolon blue, zolon red, and silver nitrate in 50 per cent methanol-water were made up containing 0.0005 mole per liter. Solutions suitable for visible spectra were made up by diluting one-milliliter samples of zolon blue and zolon red solutions to 25 ml. with 50 per cent methanol-water. A solution of the silver-zolon red complex was made up from one-milliliter samples of zolon red and silver nitrate stock solutions diluted to 25 ml. Spectra were run from 400 to 800 millimicrons using quartz cells in the Cary spectrophotometer.

Infrared spectra. Infrared spectra of zolon red, zolon blue, and the silver-zolon red complex were determined by means of the potassium bromide disk technique[9,10] on a Perkin-Elmer Model 21 infrared spectrophotometer.

Continuous variation study. The combining ratio of the silver-zolon red complex was determined by the method of continuous variations described by Job.[11] To one-milliliter samples of the 0.0005 *molar* silver nitrate stock solution 0.1- to 3-ml. samples of the 0.0005 *molar* zolon red stock solution were added and the resulting solutions were diluted to 25 ml. with 50 per cent methanol-water. The absorbance of each of these samples then was determined on the Beckman Model DU spectrophotometer at 620 millimicrons. The combining ratio was obtained from a plot of the absorbance against the molar ratio of zolon red to silver ion (Fig. 1).

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(9) M. M. Stimson and M. J. O'Donnell, *J. Am. Chem. Soc.*, **74**, 1805 (1952).

(10) U. Schiedt and H. Reinwein, *Z. Naturforsch.*, **7b**, 270 (1952).

(11) P. Job, *Ann. chim.*, [10] **9**, 113 (1928).

The Preparation of Bis-(ethyl 3,5-dimethylphenoxyacetate)-4,4'-disulfide[1]

C. S. MARVEL, THOMAS H. SHEPHERD, CHARLES KING, JAMES ECONOMY, AND EUGENE D. VESSEL

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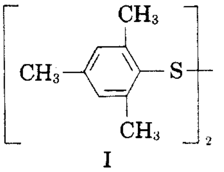
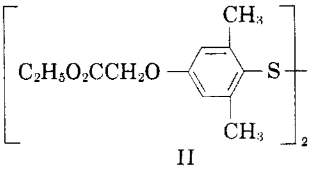
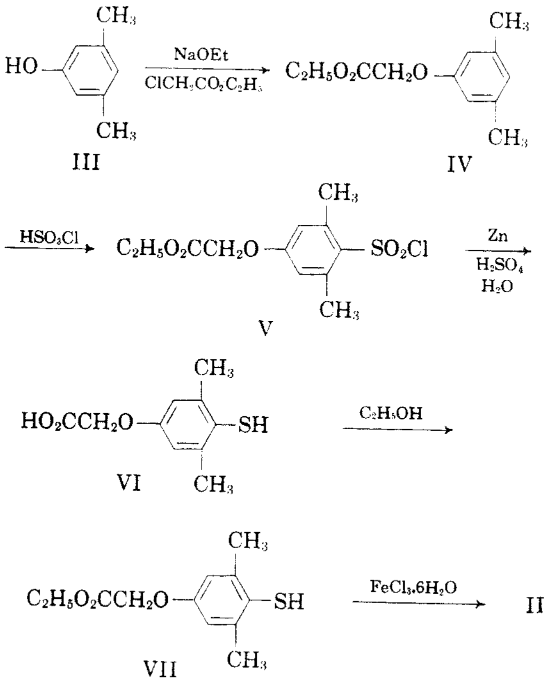
In a recent publication[2] it was shown that dimesityldisulfide (I) was an effective bis-type modifier in the emulsion polymerization of butadiene. This modifier lacks the reactive group needed to test thoroughly the usefulness of such modifiers in making synthetic rubber vulcanizates of improved resilience. This paper describes the preparation of bis-(ethyl 3,5-dimethylphenoxyacetate)-4,4'-disulfide (II) which does have an ester group as the active group needed in the modified polymer.


I


II

The following five step synthesis has been accomplished in an over-all yield of about 30%:



The chlorosulfonation reaction (step 2) might produce isomeric materials but it appears to give a single material which is assumed to be the isomer with the sulfonyl chloride group *para* to the ether oxygen. In the reduction step some of the chlorosulfonyl group is removed by hydrolysis and the ester group is hydrolyzed. Thus a re-esterification is needed.

The disulfide has a modifier effectiveness (in bulk styrene) which is very similar on a molar basis to that of other 2,6-dimethylphenyldisulfides.[3]

The chlorosulfonation of 3,5-dimethylphenoxyacetic acid and the oxidation of 4-mercapto-3,5-dimethylphenoxyacetic acid to the disulfide are also reported.

EXPERIMENTAL

Preparation of ethyl 3,5-dimethylphenoxyacetate. To a 3000-ml. three-necked flask fitted with a stirrer and reflux condenser was added 500 ml. of ethanol and 24 g. (1.0 mole) of sodium. After the sodium had dissolved, a solution of 112 g. of 3,5-dimethylphenol in 200 ml. of ethanol was added, and the solution was stirred for 15 minutes. A solution of 122 g. (1.0 mole) of ethyl chloroacetate then was added, and the mixture was heated under reflux for 4–6 hours and allowed to stand overnight. A solution of 6 g. of sodium in 100 ml. of ethanol was added, followed by 30 g.

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(1) The work discussed herein was performed as a part of the synthetic rubber research project sponsored by the National Science Foundation.

(2) A. J. Costanza, R. J. Coleman, R. M. Pierson, C. S. Marvel, and Charles King, *J. Polymer Sci.*, **17**, 319 (1955).

(3) Private communication from Mr. R. M. Pierson.