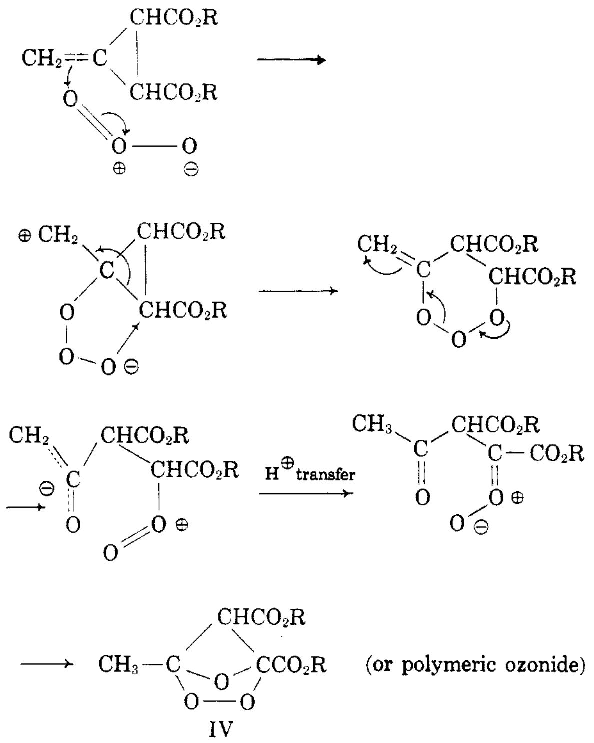

yield ethyl acetoxaloacetate and no formaldehyde as expected of esters of II.[8] However, it should be noted that methylenecyclopropane yields but 2% of formaldehyde on ozonization.[9] Furthermore, if attack of ozone is electrophilic in character, esters of I might afford acetoxaloacetates by a sequence of reasonable reactions like the following (here presented in condensed form) which involves a rather common type of ring-opening process as the key step. IV can be regarded as the normal ozonide of II.

We are indebted to Dr. Martin G. Ettlinger for helpful discussions and generous samples of I and III.

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A Note on the Dechlorination Condensation of Benzal Chloride and Benzotrichloride by Iron and Water

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Several years ago, one of the authors reported on the dechlorination condensation by iron powder suspended in water, whereby dibenzyl was produced from benzyl chloride, *trans*-stilbene (II) from benzal chloride, and *trans*-α,α'-dichlorostilbene (IV) from benzotrichloride.[1] This procedure has been applied by several other investigators to the condensation of *p*-(α-halogenoalkyl)anisoles[2] and their derivatives,[3,4] to prepare hexestrol and its derivatives.

$$2\,C_6H_5CHCl_2 \xrightarrow{Fe + H_2O} \underset{\text{I}}{C_6H_5CHCl\text{—}CHClC_6H_5} \xrightarrow{Fe + H_2O} \underset{\text{II}}{C_6H_5CH{=}CHC_6H_5} \quad (A)$$

$$2\,C_6H_5CCl_3 \xrightarrow{Fe + H_2O} \underset{\text{III}}{C_6H_5CCl_2\text{—}CCl_2C_6H_5} \xrightarrow{Fe + H_2O} \underset{\text{IV}}{C_6H_5CCl{=}CClC_6H_5} \quad (B)$$

It is natural to consider that the reaction of benzal chloride or benzotrichloride proceeds *via* path (A) or (B), respectively.

The present paper describes the isolation of the intermediate α-stilbene dichloride (I) and tolane tetrachloride (III) in the very early stages of the dechlorination reaction of benzal chloride and benzotrichloride, respectively. Moreover, it has been ascertained that intermediate (I) on the further dechlorination with iron gave *trans*-stilbene (II) and intermediate (III) gave *trans*-α,α'-dichlorostilbene (IV). These condensations probably proceed by way of unstable organoiron chlorides as in the case of magnesium or zinc. But the organoiron compounds are so unstable and highly reactive toward another chlorine atom that they are difficult to detect. It is of interest to note that the organoiron intermediate hardly reacts with water, and this property differentiates it from the organomagnesium or organozinc compound. The role of the water in the reaction is not only to keep the fluidity of the mixture but to prevent the occurrence of Friedel-Crafts reactions leading to polymeric substances.

EXPERIMENTAL

All melting points are corrected. The syntheses under optimum conditions are described.

α-Stilbene dichloride (I) *from benzal chloride.* In a flask equipped with a reflux condenser were placed water (200 cc.) and finely divided iron (reduced iron powder) (35 g., 0.632 mole). The flask was dipped in a boiling water-bath and to it was added benzal chloride (50.9 g., 0.316 mole) with vigorous stirring in one minute. The stirring then was continued for 3 minutes. The reaction mixture was extracted with benzene and the solvent was evaporated to dryness to produce crude material. The crude crystals were washed with petroleum ether, aqueous ammonia, and then

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

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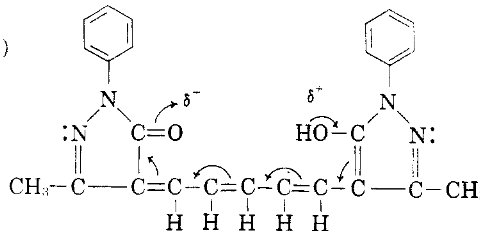
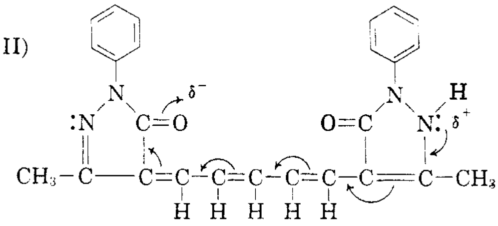
The monomethine oxonol derived from 1-phenyl-2-methyl-pyrazolone-5 was described by Knorr.[2] Later, dyes such as zolon blue, (I), which contain the (—CH=CH—)$_n$ group were prepared and their chromophoric activity discussed.[3] While working with zolon blue Gehauf and Goldenson[1] found that treatment 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:

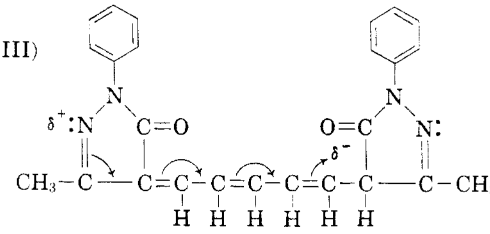
(I)



(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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