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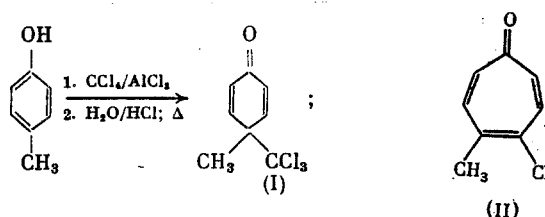
POSSIBILITY OF THE FORMATION OF CHLOROSUBSTITUTED TROPONE RINGS
UNDER ZINCKE-SUHL REACTION CONDITIONS

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The reaction of *p*-cresol with CCl_4 in the presence of AlCl_3 leads to the formation of 4-methyl-4-trichloromethyl-2,5-cyclohexadien-1-one (I) in 18% yield [1]. As a consequence, this reaction has been used commonly as the major method for the synthesis of CCl_3 -substituted cyclohexadienones [2]. This reaction has been assumed to proceed through electrophilic ipso attack of the benzene ring by cation of the intermediate $\text{CCl}_3^+\text{AlCl}_4^-$.

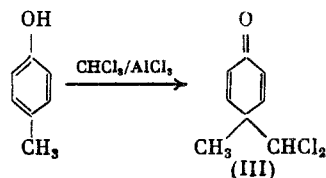
For a more complete understanding of the nature of this reaction and the reactivity of the para-semiquinoid species (I) generated [3], it is important to gain information on accompanying and side reactions. Merchant and Jadhav [2] have previously noted only the formation of polysubstituted benzoid aromatic derivatives. In the present work, we were the first to discover that traces of a nonbenzoid compound, namely, 4-methyl-5-chloro-2,4,6-cycloheptatrien-1-one (II), which could be isolated by taking large quantities of the starting reagents, were also formed under standard Zincke-Suhl reaction conditions.



It is interesting to note that a detailed study of the total composition of the products in an another method for the synthesis of halomethyl-substituted cyclohexadienones, namely, the "anomalous Reimer-Tiemann reaction," which we have termed the Auwers reaction [4], proceeding through the action of $\text{CHCl}_3/\text{KOH}/\text{H}_2\text{O}$ on *p*-cresol and leading to the formation of 4-methyl-4-dichloromethyl-2,5-cyclohexadien-1-one (III) as the major product, also led to the formation of trace amounts of tropone derivatives, including a compound directly generated from the starting *p*-cresol by the action of dichlorocarbene and not containing chlorine in the seven-membered ring [5]. The formation of chloro derivative (II) in our reaction, in principle, may be related to the possibility of the intermediate formation of carbene species such as $[\text{CCl}_2][\text{AlCl}_3 \cdot \text{Cl}_2]$ (the aromatic *p*-cresol ring acts as a trap in this case) or cyclo- $\text{C}(\text{O})(\text{CH}=\text{CH})_2\text{C}(\text{CH}_3)\text{CCl}$ [6] or related to oxidative ring expansion in the intermediate carbocationic species, cyclo- $\text{C}(\text{O})(\text{CH}=\text{CH})_2\text{C}(\text{CH}_3)\text{CCl}_2^+$ according to rearrangements known for the corresponding gem- CH_2Hal -substituted derivatives and described by Cook and Koptug [7]. The participation of CHCl_3 (as an impurity in the CCl_4 sample) may be excluded since we have found that the reaction of *p*-cresol with CHCl_3 and a two-fold excess of AlCl_3 under the same

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conditions gives a small amount of dienone (III) and is not accompanied by troponization. We should note



that it had been impossible to detect any products when this reaction was carried out in the presence of a 30% excess of AlCl_3 ; the corresponding CHBr_2 derivative was obtained only in the case of CHBr_3 [8].

In light of the formation of disubstituted tropone (II) in high yield, which we recently detected in the redox-troponization of dienone (I) by the action of $\text{Pd}(\text{PPh}_3)_4$, featuring the reductive expansion of the six-membered ring semiquinoid ring [9], the results of this work confirm the new chemical interrelationships studied between semiquinoid [3] and nonbenzoid aromatic systems [4, 9] and may be useful in providing a detailed theoretical interpretation of the reaction mechanism of both these types of compounds.

EXPERIMENTAL

The PMR spectra were taken on a Bruker WP-200 SY spectrometer at 200 MHz with TMS as the standard. Chemapol 40/100 μ silica gel was used for column chromatography, while Silpearl UV-254 (0.26 μ) was used for the preparative thin-layer chromatography. The R_f values of the products studied were determined on Silufol UV-254 plates with 1:1 benzene-ether as the eluent. Pure-grade p-cresol, chemically-pure grade CCl_4 and CHCl_3 , and pure-grade granulated AlCl_3 were used as the reagents.

4-Methyl-5-chloro-2,4,6-cycloheptatrien-1-one (II). The reaction mixture obtained from 1.38 moles p-cresol, 7.7 moles CCl_4 , and 2.76 moles AlCl_3 according to Zincke and Suhl [1] was subjected to steam distillation over 30 h to give a portion of the major reaction product, namely, 4-methyl-4-trichloromethyl-2,5-cyclohexadien-1-one (I) (39 g, 12%) and about 8 liters of an aqueous layer. After separation of the crystals of dienone (I), this layer was extracted with 24 \times 70-ml portions of CHCl_3 . The solvent was distilled off and the residue was subjected to chromatography on a silica gel column in order to separate the major portion of p-cresol and dienone (I) (R_f 0.5-0.6). The combined fractions with R_f less than 0.5 were additionally purified by thin-layer chromatography on silica gel-coated glass plates using 1:1 benzene-ether as the eluent to give 0.007 g tropone (II) (R_f 0.22). Mass spectrum, m/z (relative intensity, %): 154 (20) $[\text{M}]^+$, 126 (21) $[\text{M}-\text{CO}]^+$, 91 (100) $[\text{M}-\text{CO}-\text{Cl}]^+$. The PMR spectrum obtained for this compound coincided with that reported in our previous work [9].

4-Methyl-4-dichloromethyl-2,5-cyclohexadien-1-one (III). A sample of 51.8 g (0.4 mole) AlCl_3 was added in portions with stirring to a solution of 24.8 g (0.23 mole) p-cresol in 100 ml (1.24 mole) CHCl_3 at 50-60°C over 1.3 h and maintained for 2.5 h at this temperature. The mixture was carefully decomposed by the addition of 120 ml 10% hydrochloric acid and the major portion of unreacted p-cresol was distilled off by steam distillation. The steam distillation of the mixture was then continued into another receiver over 3 h and the aqueous distillate (about 1 liter) was extracted with CHCl_3 . The extract was distilled off. The residue was treated with aqueous KOH and extracted with benzene. The benzene solution was distilled off and the residue was recrystallized from heptane to give 0.083 g (0.2%) dienone (III), mp 52°C. The PMR spectrum of this product coincided with the data of Vitullo [10].

CONCLUSIONS

1. The formation of trace amounts of a chloro-substituted nonbenzoid aromatic derivative, namely, 4-methyl-5-chloro-2,4,6-cycloheptatrien-1-one under standard Zincke-Suhl reaction conditions, was detected.
2. The possibility was demonstrated for the formation of the product of the "anomalous Reimer-Tiemann reaction" (Auwers reaction), namely, 4-methyl-4-dichloromethyl-2,5-cyclohexadien-1-one in a Zincke-Suhl-type reaction using CHCl_3 instead of the usual reagent, CCl_4 .

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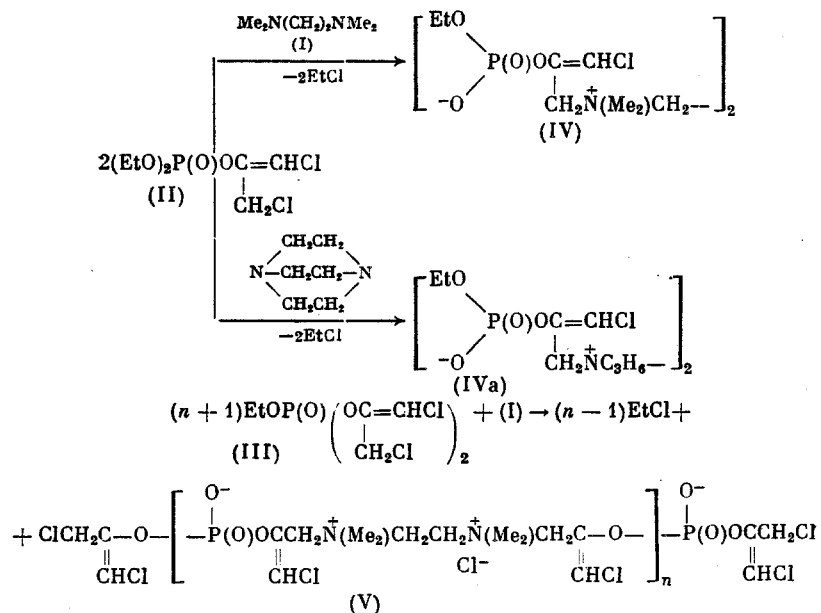
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BIS- AND POLYBETAINES OF PHOSPHORUS-CONTAINING VINYLCHOLINES

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In a search of new types of physiologically active phosphorus compounds soluble in water and resistant to hydrolysis, we developed a method for the preparation of phosphorus-containing betaines with an ammonium group in the substituted vinyl ester group [1]. This method is applicable for the synthesis of previously unknown bis- and polybetaines. This reaction is based on the alkylation of bisamines such as tetramethylethylenediamine (I) and triethylenediamine by O-phosphorylated allyl chlorides (II) and (III). The initially obtained tri-alkyl esters are dealkylated upon heating to betaines (IV) and (V).



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