

meter of 10 nm and an inner diameter of 8 mm. The resin bed was supported by a perforated plate of stainless steel covered with glass wool and Celite. The dimensions of the resin bed were 8×750 mm. The resin (Dowex 21 K) was classified as usual and used in its sulfate form. The solution was fed onto the top of the column by means of a high-pressure piston-type pump. The pressure drop in the column was about 15 kp/cm^2 . The flow rate was $0.8 \text{ ml cm}^{-2} \text{ min}^{-1}$. In other respects the working conditions were the same as reported earlier.²

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The Configuration of N-Methyl-*p*-chlorobenzaldoxime

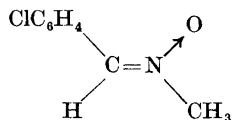
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The configuration of the N-methyl derivative of oximes has been previously studied by chemical methods. Methylation by use of dimethyl sulfate, which has never yielded both of the theoretically possible N-methyl isomerides has been reported to yield the isomers with the "anti" configuration.^{1,2} On the other hand, use of diazomethane as a methylating agent is stated to yield the same N-methyl isomers from the "syn" oximes, but different N-methyl isomers from the "anti" oximes.³

We have prepared N-methyl-*p*-chlorobenzaldoxime by methylating "syn" *p*-chlorobenzaldoxime with dimethyl sulfate;⁴ after repeated crystallization from benzene the m.p. was $128-129.5^\circ$, and the formula $\text{ClC}_6\text{H}_4\text{NO}$ was confirmed by micro-analysis.

The crystal structure of the compound was determined by a three dimensional X-ray diffraction study, the result of which showed conclusively that the N-methyl-*p*-chlorobenzaldoxime has the "anti" configuration,



The positions of the hydrogen atoms were revealed by a threedimensional difference Fourier synthesis. The molecular dimensions as found after least-squares refine-

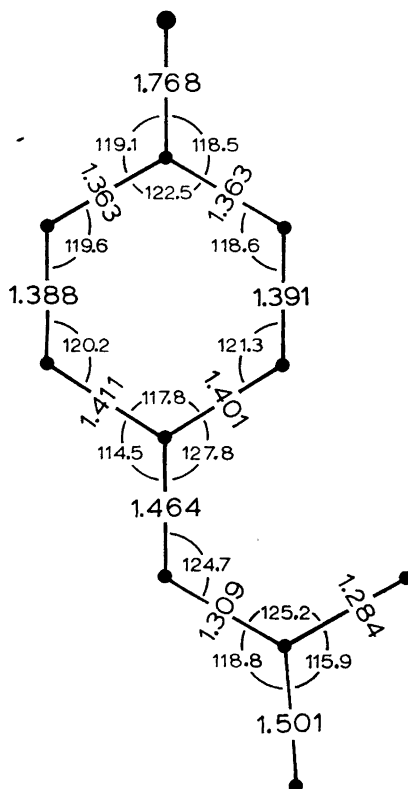


Fig. 1.

ment using individual anisotropic thermal parameters for all atoms except the hydrogens are indicated in Fig. 1. The molecule is essentially planar, except for the nitrogen, oxygen and methylcarbon, which are removed 0.17, 0.22 and 0.24 Å, respectively, from the plane through the benzene ring; it is somewhat surprising that the deviation of the oxime group from the molecular plane is so comparatively small, since in "anti" *p*-chlorobenzaldoxime the nitrogen and oxygen atoms were found to be removed 0.36 and 0.76 Å, respectively, from a plane through the benzene ring.⁵ The N→O bond is, as might be expected, much shorter than the N—O distances found in oximes and amine oxide hydrochlorides.

A full description of the structure determination will appear elsewhere.

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Electroorganic Preparations

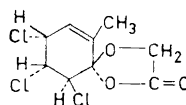
XIV. Reduction of a Chlorinated Cyclohexene Derivative

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On chlorination of *o*-cresoxyacetic acid in an organic solvent a small quantity of a neutral fraction is obtained. The main component of this material has been shown

to have the constitution A.¹ The absolute configuration has been established by X-ray structure analysis.² The compound is a cyclic ester-ketal of 2-methyl-4,5,6-trichlorocyclohex-2-en-1-one with glycolic acid.



Compound A

The compound is polarographically reducible. In aqueous solution the wave is drawn out and ill-defined. It starts around -0.2 V *vs* S.C.E. and covers about 1 V. When alcohol is added the wave becomes better defined, and when the alcohol content is increased to 40 % to 50 % an S-shaped wave with a small prewave is obtained. The half-wave potential becomes more negative with increasing alcohol content. For a polarographic determination of the compound a neutral solution containing 45 % alcohol and 1 M potassium chloride is recommended.

The half-wave potential is independent of pH from pH 1 to pH 9. In strongly acid solution the wave is covered by the reduction of hydrogen ions and in alkaline solution the dioxolone ring is opened¹ with the formation of the polarographically inactive 4,6-dichloro-2-methylphenol. The half-wave potential of the compound in 45 % alcohol is -1.05 V *vs* S.C.E.

The electrode reaction in slightly acid and neutral medium containing 45 % alcohol was shown by controlled potential reduction to be a four electron reduction and the isolated products were *o*-cresoxyacetic acid and chloride ions according to the reaction scheme given below. The reduction thus involves the cleavage of three carbon-chlorine bonds and one carbon-oxygen bond.

The polarographic reduction of a polyhalogen compound can either be a stepwise reduction as in the reduction of carbon tetrachloride³ or the simultaneous cleavage of two or more carbon-halogen bonds as in 2,3-dibromobutane,³ 3-trifluoromethyl-4,6-disulfamylaniline,⁴ or γ -hexachlorocyclohexane.⁵

