

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.<sup>5</sup> 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.

1. Brady, O. L. and Dunn, F. P. *J. Chem. Soc.* **1926** 2411.
2. Sutton, L. E. and Taylor, T. W. *J. Chem. Soc.* **1931** 2190.
3. Thompson, A. F., Jr. and Baer, M. *J. Am. Chem. Soc.* **62** (1940) 2095.
4. Brady, O. L., Dunn, F. P. and Goldstein, R. F. *J. Chem. Soc.* **1926** 2387.
5. Jerslev, B. *Thesis* (Dansk Farmaceutforening, Copenhagen) 1958, p. 66.

Received October 2, 1963.

## Electroorganic Preparations

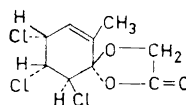
### XIV. Reduction of a Chlorinated Cyclohexene Derivative

HENNING LUND

Department of Chemistry, University of Aarhus, Aarhus, Denmark

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.<sup>1</sup> The absolute configuration has been established by X-ray structure analysis.<sup>2</sup> The compound is a cyclic ester-ketal of 2-methyl-4,5,6-trichlorocyclohex-2-en-1-one with glycolic acid.



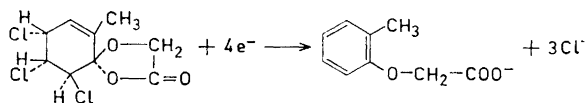
Compound A

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 opened<sup>1</sup> 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 tetrachloride<sup>3</sup> or the simultaneous cleavage of two or more carbon-halogen bonds as in 2,3-dibromobutane,<sup>3</sup> 3-trifluoromethyl-4,6-disulfamylaniline,<sup>4</sup> or  $\gamma$ -hexachlorocyclohexane.<sup>5</sup>



The electrode reaction of compound A reminds mostly of that of  $\gamma$ -hexachlorocyclohexane<sup>5</sup> which in a six electron reduction is reduced to benzene and chloride ions. The half-wave potential of the latter is about 0.5 V more negative than that of compound A. This is not unexpected as more energy is required to transform a cyclohexane ring into a benzene ring than to form a benzene ring from a cyclohexene ring.

A further resemblance between  $\gamma$ -hexachlorocyclohexane and compound A is that when the chlorine-containing half-part of the 6-ring in compound A is inverted (*i.e.* by operation of a two-fold axis and a reflection in a mirror plane) and combined with the original half-part the molecule formed is  $\gamma$ -hexachlorocyclohexane.

*Experimental. Reduction of compound A.* A suspension of 1.00 g of compound A was reduced in an acetate buffer pH 5 containing 45 % alcohol at a cathode potential of  $-1.2$  V vs S.C.E. The electron consumption was 4 electrons per molecule. In the reduced solution a chloride ion concentration corresponding to 2.8 Cl<sup>-</sup>/mole compound A was found. Possibly some chloride ions are lost into the agar bridge by migration during the reduction. Most of the solvent was evaporated *in vacuo* and on addition of hydrochloric acid a precipitate, 0.50 g, was obtained. It was identified as *o*-cresoxyacetic acid by its m.p. 154° and the I.R.-spectrum.

1. Lund, Hakon *Acta Chem. Scand.* **12** (1958) 793.
2. Haagensen, C. O. and Danielsen, J. *Abstract of Communications, Intern. Union of Crystallography, 6th Intern. Congr. and Symposia, Rome Sept. 1963.*
3. Stackelberg M. v. and Stracke, W. *Z. Elektrochem.* **53** (1949) 118.
4. Lund, Henning *Acta Chem. Scand.* **13** (1959) 192.
5. Schwabe, K. and Frind, H. *Z. physik. Chem.* **196** (1951) 342.

Received August 24, 1963.

## The Preparation and the Rearrangement of 1,1-Dibromobutanone-2

CHRISTOFFER RAPPE

*Institute of Chemistry, University of Uppsala, Uppsala, Sweden*

1,1-Dibromo methyl ketones,  $\text{CHBr}_2\text{COCH}_2\text{R}$ , cannot be prepared by the acid catalyzed bromination of the corresponding ketone.<sup>1</sup> In this reaction the main product is the symmetric dibromoketone,  $\text{CH}_2\text{BrCOCHBrR}$ ; in one case a low yield of  $\text{CH}_3\text{COCBr}_2\text{R}$  is also reported.<sup>2</sup>

Wagner and Moore prepared some tribromo ketones,  $\text{CHBr}_2\text{COCBrRR'}$ , by treating the diazo ketone,  $\text{CHN}_2\text{COCHRR'}$ , with two moles of bromine.<sup>3</sup> In the present investigation diazo ketones and one mole of bromine have been found to give 1,1-dibromo methyl ketones. The yield of 1,1-dibromobutanone-2 was 50 % and that of 1,1-dibromopentanone-2 was 45 %. This is apparently a convenient method of synthesizing such compounds.

The former product was analyzed by means of NMR-spectroscopy. Even after two distillations it was not possible to obtain the bromo ketone in a pure state. Only 90 % consisted of 1,1-dibromobutanone-2, the remainder consisting of 1-bromobutanone-2 (6 %) and 1,3-dibromobutanone-2 (4 %). When the crude product was left for 15 h prior to distillation the main product was 1,3-dibromobutanone-2. This indicates that a rearrangement occurs during this time.

It has recently been observed that 1,1-dibromoacetone is easily rearranged.<sup>4</sup> At equilibrium, a sample of 1,1-dibromoacetone kept at 30°C in the dark contains 13 % of monobromoacetone, 6 % of 1,1-dibromoacetone, 67 % of 1,3-dibromoacetone and 14 % of 1,1,3-tribromoacetone.<sup>5</sup>

A sample of 1,1-dibromobutanone-2 was treated as above and it was also found to rearrange. The rearrangement was followed by recording NMR-spectra at intervals. In Fig. 1 the amounts of the bromo ketones formed are plotted against time. Already after 9 h the main component in the sample is the 1,3-dibromo ketone.

Bromoketones are known to undergo a bromine rearrangement catalyzed by hydrogen bromide; see Ref.<sup>6</sup> where further references are collected. In the present