The electrode reaction of compound A reminds mostly of that of \( \gamma \)-hexachlorocyclohexane\(^2\) 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\(^-\)/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\(^\circ\) and the I.R.-spectrum.


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

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1,1-Dibromo methyl ketones, CHBr\(_2\)COCH\(_2\)R, cannot be prepared by the acid catalyzed bromination of the corresponding ketone.\(^1\) In this reaction the main product is the symmetric dibromoketone, CH\(_3\)BrCOCHBrCH\(_2\)Br; in one case a low yield of CH\(_3\)COBr\(_2\)CH\(_2\)R is also reported.\(^2\)

Wagner and Moore prepared some tribromo ketones, CHBr\(_2\)COCHBr\(_2\)R, by treating the diazo ketone, CH\(_2\)N=C=NCH\(_2\)COCH\(_2\)R, with two moles of bromine.\(^3\) 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-dibromoaacetone is easily rearranged.\(^4\) At equilibrium, a sample of 1,1-dibromoaacetone kept at 30°C in the dark contains 13 \% of monobromoaacetone, 6 \% of 1,1-dibromoaacetone, 67 \% of 1,3-dibromoaacetone and 14 \% of 1,3,3-tribromoaacetone.\(^5\) 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.\(^4\) where further references are collected. In the present
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1,1-Dibromopentanone-2. The synthesis was performed as above; 9.8 g of diazomethane in 750 ml of ether, 8.3 g of butyryl chloride and 12.5 g of bromine gave 9.6 g of 1,1-dibromopentanone-2, b.p. 73–76°C at 10 mm, nD^25 = 1.5030, purity 90 % (NMR).

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Monoalkylsulfamyl Chlorides

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In the search for new compounds with possible drug action intermediates with the constitution RNHSO_2Cl (R being lower alkyl) were desirable. Although the corresponding dialkylsulfamyl chlorides R_NSO_2Cl have been known for nearly a century, and the unsubstituted sulfamyl chloride for some years, monoalkylsulfamyl chlorides do not seem to be described. As dialkylsulfamyl chlorides can be made by the reaction between sulfuryl chloride and the hydrochlorides of lower secondary amines, a similar reaction might be expected to take place when the hydrochloride of a primary amine is used. In fact this was found to be the case with the normal C_3—C_5 alkyl amines. When the hydrochlorides of methyl-, hexyl-, cyclohexyl-, and octylamine were used the yields were too low to permit the isolation of monoalkylsulfamyl chlorides. That at least methylsulfamyl chloride was formed can be concluded from the fact that N-methyl-N'-propylsulfamide could be ob-