

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.

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

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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  $\text{CH}_3\text{COCHBr}_2\text{R}$  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

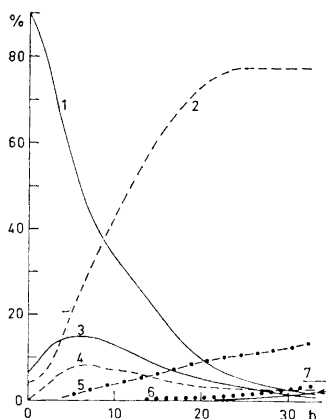


Fig. 1. Percentage of bromo ketones plotted versus time (in hours) for the rearrangement of 1,1-dibromobutanone-2. 1,  $\text{CH}_3\text{CH}_2\text{COCHBr}_2$ ; 2,  $\text{CH}_3\text{CHBrCOCH}_2\text{Br}$ ; 3,  $\text{CH}_3\text{CH}_2\text{COCH}_2\text{Br}$ ; 4,  $\text{CH}_3\text{CHBrCOCHBr}_2$ ; 5,  $\text{CH}_3\text{CHBrCOCH}_3$ ; 6,  $\text{CH}_3\text{CBr}_2\text{COCH}_2\text{Br}$ ; 7,  $\text{CH}_3\text{CBr}_2\text{COCH}_3$ .

case it was also found that the addition of hydrogen bromide catalyzed the rearrangement. 16.6 mg of 66% hydrobromic acid were added to 1.18 g of 1,1-dibromobutanone-2. Already after 5 h 1,3-dibromobutanone-2 was the main component in this sample.

The variety of products indicates that the rearrangement is complex. A discussion of the different reactions taking part will be published elsewhere together with a discussion of the rearrangement of 1,1-dibromoacetone.

*Experimental.* The NMR-spectra were recorded on a Varian Associates Model A 60 spectrometer.

*1,1-Dibromobutanone-2.* To 10.0 g of diazomethane in 680 ml of ether, 7.4 g of propionyl chloride dissolved in 100 ml of ether were added dropwise under stirring. After standing for 24 h one third of the ether was distilled off together with the excess of diazomethane. 13.0 g of bromine dissolved in 20 ml of carbon tetrachloride were added, the organic layer was washed with water, the solvents were distilled off at reduced pressure and the crude product was distilled at once. A fraction, 10.3 g, b.p. 60–64°C at 8 mm, was collected. On redistillation the b.p. 63–65°C at 9 mm and  $n_D^{25} = 1.5112$  were obtained.

*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,  $n_D^{25} = 1.5030$ , 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  $\text{RNHSO}_2\text{Cl}$  (R being lower alkyl) were desirable. Although the corresponding dialkylsulfamyl chlorides  $\text{R}_2\text{NSO}_2\text{Cl}$  have been known for nearly a century,<sup>1,2</sup> and the unsubstituted sulfamyl chloride for some years<sup>3</sup> 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<sup>2,4</sup> 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  $\text{C}_2$ – $\text{C}_8$  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-