yield of 5.2 g of tan-colored crystals, m.p. 142-147°C (yield 70 %), was obtained. Repeated recrystallization from carbon tetrachloride gave faint yellow crystals, m.p. 155-156°C. (Found: C 23.64; H 1.55; Br 62.61; Calc. for C₆H₃Br₂O₂: C 23.47; H 1.58; Br 62.45).

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Proton Mobility of α-Haloketones
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My primary interest was to explain the results of the halogenation of certain ketones and haloketones.1-4 In this connection it is necessary to determine the mobilities of protons within some pertinent ketones and between the same ketones.

NMR-spectroscopy has proven to be an excellent tool for these studies. Since all α-protons can be exchanged by deuterium in an acid catalyzed reaction,7 a solution was prepared from acetyl chloride and heavy water8 (solution A), and the haloketones were treated with an excess of this solution. Only one-phase systems were studied. The protium-deuterium exchange was studied at various time intervals. In addition the time was estimated when the area under the increasing OH-peak of the δ-acid was the same as the sum of the areas under all α-C−H-peaks; i.e. half of the α-protons in the haloketone had exchanged, (D/H = 1). The time for various halo-

ketones is given in Table 1. It was rather independent of the exact proportions of the components if a sufficient excess of deuterium was present; see runs 6 and 7, Table 1.

The parent unhalogenated ketones had the shortest exchange times. The introduction of one, two or three halogens decreases the proton-mobility. No significant difference between the halogens are observed. The low value of 1,1-dibromacetoacetone can be explained by the acid catalyzed rearrangement of this haloketone to 1,3-dibromoacetone.4 Deuterium seems to be introduced in the molecule during the rearrangement.

The relative mobility of protons within a molecule can be studied by estimating the ratio of protons in α- and α'-position (a/a') at various time intervals. In Table 1 these ratios are given for some compounds at the time D/H = 1. In the beginning of the reaction the ratio for monohaloacetones is 1.5, for 1,1-dihaloacetones 3.0 and for 1,1,3-trihaloacetones 2.0.

It is interesting to note that the ratios (a/a') for monohaloacetones are much greater than 1.5, for 1,1-dihaloacetones nearly unchanged, and for 1,1,3-trichloroacetone smaller than 2. This means that the protons in groups with one halogen have a greater mobility than protons in non- or dihalogenated groups. Taking into account the statistical factor the mobility of a CH₂X-proton is about twice that of a CH₃-proton or CHX₂-proton, which are about the same.

From these results it can be postulated that halogenation of monohaloacetones will preferentially give the 1,1-dihalo- instead of the 1,3-dihaloacetone.1,8

In addition the results of the halogenation of 1,1-dichloroacetones can be explained from the results of this investigation.5,4

Secondary rearrangement influence the isolated polybromo ketones.5,8

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Studies on Alkylsulfinylcarboxylic Acids

IV. The Reduction of cis- and trans- \( \beta \)-Ethylsulfinylcrotonic Acids by Means of Iodide in Acid Solution

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The two isomeric \( \beta \)-ethylethiocuproic acids (I and II)* have previously been studied by some authors,\(^3\,4\) but the corresponding sulfanyl- and one of the sulfonyle- acids have not been reported. In order to obtain further information concerning the mechanism of the reduction of \( \beta \)-alkylsulfinylcarboxylic acids in acidic iodide solution, the two geometric isomers of \( \beta \)-ethylsulfinylcrotonic acid were regarded as suitable compounds for study. As an explanation for the great reactivity of the saturated \( \beta \)-compounds in this reaction, the for-

* The figures refer to the experimental part of this work.