yield of 5.2 g of tan-coloured 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 $C_5H_4Br_2O_2$: C 23.47; H 1.58; Br 62.45).

Acknowledgements. Thanks are due to Professor Arne Fredga for his interest in this work and for all facilities placed at my disposal. The micro analyses were done by Dr. A. Bengtsson.

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Received January 23, 1965.

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.[1-6] In this connection it is necessary to determine the mobilities of protons within some pertinent ketones and between the same ketones.

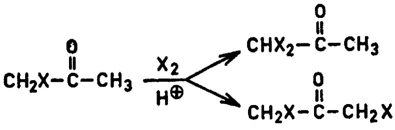
NMR-spectroscopy has proven to be an excellent tool for these studies. Since all α-protons can be exchanged by deuterium in an acid catalyzed reaction,[7] a solution was prepared from acetyl chloride and heavy water [8] (solution A), and the haloketones were treated with an excess of this solution. Only 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 d-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 haloketones 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-dibromoacetone can be explained by the acid catalyzed rearrangement of this haloketone to 1,3-dibromoacetone.[6] Deuterium seems to be introduced in the molecule during the rearrangement.

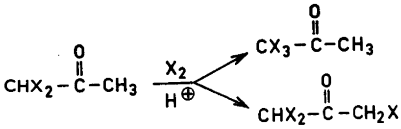
The relative mobility of protons within a molecule can be studied by estimating the ratio of protons in α- and α′-position (α/α′) at various time intervals. In Table 1 these ratios are given for some compounds at the time D/H = 1. In the beginning of the reaction the ratio for monohaloacetones is 1.5,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

It is interesting to note that the ratios (α/α′) 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 CH_2X-proton is about twice that of a CH_3-proton or CHX_2-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.[1,3-6]



$$CH_2X{-}\overset{O}{\overset{\|}{C}}{-}CH_3 \xrightarrow[H^\oplus]{X_2} CHX_2{-}\overset{O}{\overset{\|}{C}}{-}CH_3 \;+\; CH_2X{-}\overset{O}{\overset{\|}{C}}{-}CH_2X$$



$$CHX_2{-}\overset{O}{\overset{\|}{C}}{-}CH_3 \xrightarrow[H^\oplus]{X_2} CX_3{-}\overset{O}{\overset{\|}{C}}{-}CH_3 \;+\; CHX_2{-}\overset{O}{\overset{\|}{C}}{-}CH_2X$$

In addition the results of the halogenation of 1,1-dichloroacetones can be explained from the results of this investigation.[2,4]

Secondary rearrangement influence the isolated polybromo ketones.[6,9]

Table 1.

Run no.	Haloketone	Amount g	Solution A g	D/H = 1 min	α/α′
1.	CH_3COCH_3	0.120	0.614	3.5	—
2.	CH_3COCH_2Cl	0.290	1.060	10	3.9
3.	CH_3COCH_2Br	0.212	0.903	10	3.3
4.	CH_3COCH_2I	0.225	0.953	8.5	—
5.	$CH_3COCHCl_2$	0.267	1.237	165	2.8
6.	$CH_3COCHBr_2$	0.231	1.170	60	2.8
7.	$CH_3COCHBr_2$	0.217	0.734	60	2.8
8.	$CH_2ClCOCH_2Cl$	0.420	1.764	60	—
9.	$CH_2BrCOCH_2Br$	0.438	1.608	60	—
10.	$CH_2ClCOCHCl_2$	0.354	1.517	900	1.2
11.	$CH_2BrCOCHBr_2$	*	*	*	*
12.	$CH_3CH_2COCH_3$	0.140	0.662	4.5	1.7
13.	$CH_3CHBrCOCH_3$	*	*	*	*
14.	$CH_3CH_2COCH_2Br$	0.293	1.523	7	—
15.	$CH_3CHBrCOCH_2Br$	*	*	*	*

* Two phases

Experimental. NMR-spectra were recorded with a Varian model A—60 spectrometer. The compositions in the different runs are given in Table 1. The reactions were performed in NMR-tubes at 30°C.

Solution A. 25 ml of heavy water was added to 50 ml of acetyl chloride.

Acknowledgements. The author is indebted to Professor Arne Fredga for his kind interest in this work and for all falicities placed at my disposal.

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Received January 23, 1965.

Studies on Alkylsulfinylcarboxylic Acids

IV. The Reduction of *cis*- and *trans*-β-Ethylsulfinylcrotonic Acids by Means of Iodide in Acid Solution

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The two isomeric β-ethylthiocrotonic acids (I and II)* have previously been studied by some authors,[1-3] but the corresponding sulfinyl- and one of the sulfonyl-acids have not been reported. In order to obtain further information concerning the mechanism of the reduction of β-alkylsulfinylcarboxylic acids in acidic iodide solution, the two geometric isomers of β-ethylsulfinylcrotonic acid were regarded as suitable compounds for study. As an explanation for the great reactivity of the saturated β-compounds in this reaction, the for-

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