(2.0 moles) and after 400 ml of water was added, the heavier organic layer was separated and it was immediately fractionated under reduced pressure.

1,3-Dibromo-3-methylbutanone-2, yield 56 %, b.p. 91–93°3/11 mm, $n_D^{25} = 1.5166$. Wagner and Moore gave no yield, b.p. 111°C/15 mm, $n_D^{20} = 1.5178$.[3]

1,3-Dibromo-3-methylpentanone-2, yield 67%, b.p. 114–115°C/10 mm, $n_D^{25} = 1.5146$. Wagner and Moore gave no yield, b.p. 57°C/1 mm, $n_D^{20} = 1.5155$.[3]

1,3-Dibromo-3-methylheptanone-2, yield 40%, b.p. 124–127°C/11 mm, $n_D^{25} = 1.5022$. (Found: C 33.63; H 4.94; Br 55.31. Calc. for $C_8H_{14}Br_2O$: C 33.59; H 4.93; Br 55.88).

Rearrangement of dibromoketone. General procedure. To 0.1 mole of dibromoketone was added a solution of 0.8 mole of the required hydroxide in 1000 ml of water or ethanol, 0.4 mole of the carbonate, or 0.8 mole of the bicarbonate in 1000 ml of water. The mixture was thoroughly stirred and when constant titration-values against methylorange were obtained (0.2 equiv. of base consumed), the solution was extracted with ether (3 × 100 ml), acidified with hydrochloric acid and again extracted with ether (5 × 100 ml). After drying, the ether phase was evaporated *in vacuo*. The yields and composition of the crude extracts are given in Table 1.

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1. Rappe, C. *Acta Chem. Scand.* **17** (1963) 2766.
2. Rappe, C. and Adeström, R. *Acta Chem. Scand.* **19** (1965). *In press.*
3. Wagner, R. B. and Moore, J. *J. Am. Chem. Soc.* **72** (1950) 974.
4. Jones, E., Morris, R. O., Vernon, C. A. and White, R. F. M. *J. Chem. Soc.* **1960** 2349.
5. Varian, *High Resolution NMR Spectra Catalogue* No. 114. Palo Alto 1962.
6. Favorsky, A. and Wanscheidt, A. *J. prakt Chem.* [2] **88** (1915) 658.
7. Kende, A. *Org. Reactions* **11** (1960) 278.
8. Rappe, C. *Acta Chem. Scand.* **19** (1965) 31.
9. Rappe, C. and Andersson, K. *Arkiv Kemi. In press.*
10. Wagner, R. B. and Moore, J. *J. Am. Chem.* **72** (1950) 1873.

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The Bromination of 3-Bromocyclopentane-1,2-dione

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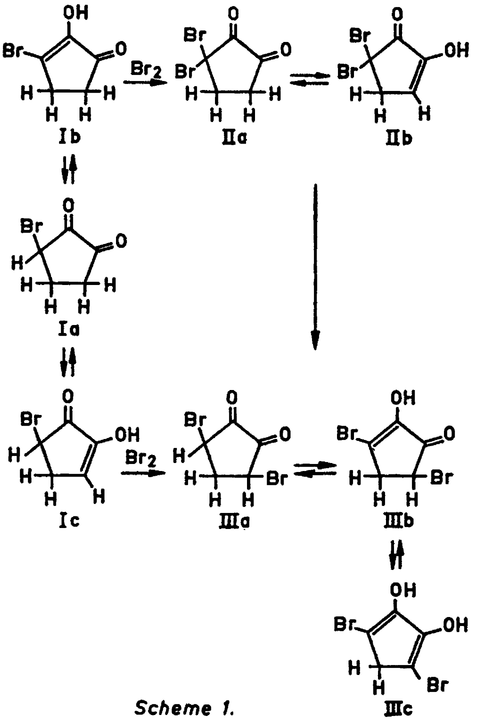
The bromination of ketones is presumed to proceed *via* the enol form.[1] 3-Bromocyclopentane-1,2-dione (Ia) is an interesting model substance for bromination studies since it already exists in its enol form, Ib.[2] From this enol the bromination should give 3,3-dibromocyclopentane-1,2-dione (IIa) or its enol form, IIb. From the other enol of 3-bromocyclopentane-1,2-dione (Ic) 3,5-dibromocyclopentane-1,2-dione (IIIa) or its enol form IIIb or IIIc would be formed, see Scheme 1.



Scheme 1.

Bromine was found to react easily with 3-bromocyclopentane-1,2-dione (Ib). From the reaction mixture a dibromoketone, $C_5H_4Br_2O_2$, could be isolated in 70 %

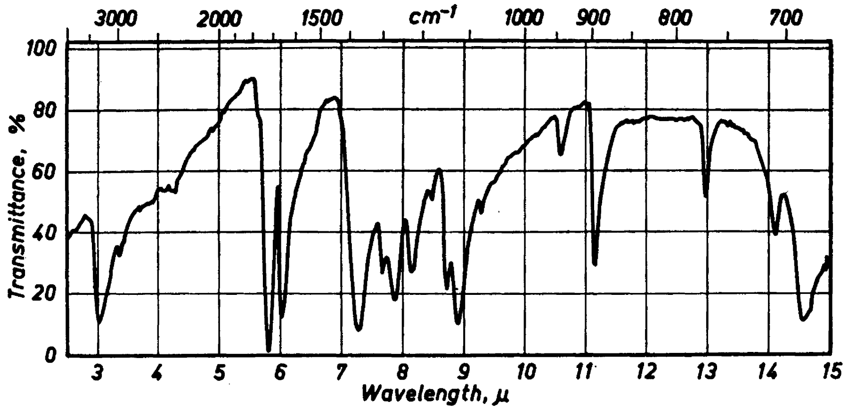


Fig. 1. Infrared spectrum of 3,5-dibromocyclopentane-1,2-dione. Solid in KBr.

yield. The substance was analyzed by infrared (Fig. 1) and by NMR (Fig. 2).

The IR-spectrum had a strong band at 6.0 µ indicating a high content of enol (IIb, IIIb or IIIc). The NMR-spectrum, recorded in acetone, DMSO, DMF and chloroform, was in all cases a typical AMX-system, with the intensity ratio 1:1:1 in agreement with structure IIIb.

From the spectrum the coupling constants could be determined: J_{cis} = 6.5 cycles/sec and J_{trans} = 2.2 cycles/sec. These values agree with the accepted values for coupling constants in rings.[3] The J_{gem} was estimated to be 18.7 cycles/sec. Further analysis of the spectrum gave 38.8 cycles/sec for the chemical shift between the two *gem* protons.

The formation of the 3,5-dibromo-compound is worth discussing. A plausible explanation of this behaviour seems to be that the 3,3-dibromoketone is formed first but then rearranges to the more stable 3,5-dibromo isomer. NMR analyses suggest that the crude reaction residue is a 50:50 mixture of IIa, a compound with an A_2B_2-system, and IIIb.

α,α-Dibromoketones do easily rearrange to the α,α′-dibromo isomer.[4,5] Although only little discussed before, this migration of bromine seems to be rather general in the preparation of α,α′-dibromoketones. The α,α-dibromoketone forms first and then rearranges to the α,α′-dibromoketone, which is the isolated product. A more detailed study of this behaviour will be given elsewhere.[6]

Experimental. The micro analyses were carried out by the Analytical Laboratory at the Chemical Institute, University of Uppsala. The NMR-spectra were recorded on a Varian model A–60 spectrometer.

3,5-Dibromocyclopentane-1,2-dione. To 5.0 g of 3-bromocyclopentane-1,2-dione[2] dissolved in 150 ml of boiling carbon tetrachloride was added 4.5 g of bromine in 10 ml of carbon tetrachloride during 30 min. After completion of the addition, 100 ml of carbon tetrachloride was distilled off, and the residue chilled. A

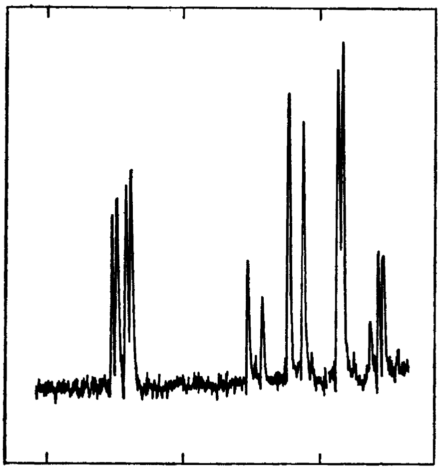


Fig. 2. NMR-spectrum of 3,5-dibromocyclopentane-1,2-dione in acetone.

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).

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1. Roberts, J. and Caserio, M. *Basic Principles of Organic Chemistry*, Benjamin, New York 1964, p. 475.
2. Rappe, C. *Acta Chem. Scand.* **19** (1965) 270.
3. Karpulus, M. *J. Chem. Phys.* **30** (1959) 11.
4. Rappe, C. *Acta Chem. Scand.* **17** (1963) 1472.
5. Rappe, C. *Acta Chem. Scand.* **17** (1963) 2140.
6. Rappe, C. *Arkiv Kemi. In press.*

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

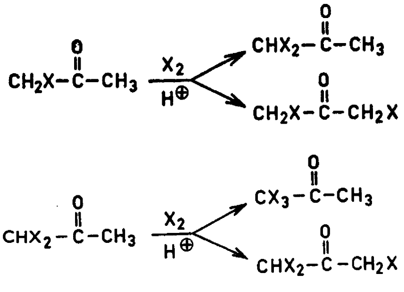
NMR-spectroscopy has proven to be an excellent tool for these studies. Since all α-protons can be exchanged by deuterium in an acid catalyzed reaction,[7] a solution was prepared from acetyl chloride and heavy water [8] (solution A), and the haloketones were treated with an excess of this solution. Only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