

## Halogenation of Ketones

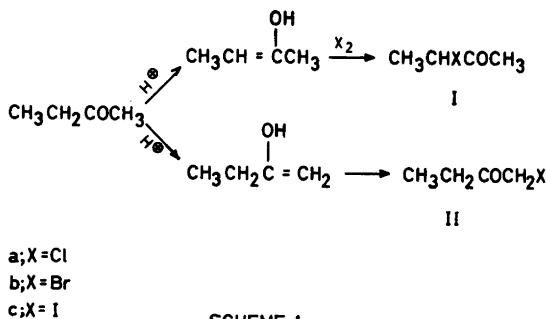
### III.\* The Sodium Acetate and Sodium Bicarbonate Catalyzed Halogenation of Butanone-2

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The acetate and bicarbonate catalyzed halogenation of butanone-2 was studied. The halogenation of ketones seems to follow three mechanisms, an acid catalyzed, a weak base catalyzed, and a strong base catalyzed. In the acetate and bicarbonate catalyzed halogenation of butanone-2, 3-halogenation occurs more readily than 1-halogenation.

The halogenation of ketones is known to proceed either by an acid or a base catalyzed reaction.<sup>1-4</sup> In the acid catalyzed bromination of butanone-2, Cardwell and Kilner<sup>5</sup> have found that the products are 3-bromo-(Ib) and 1-bromobutanone-2 (IIb) in a ratio of I/II = 2.7; see Scheme 1. On the other

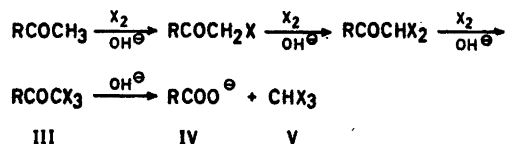


SCHEME 1

hand, the base catalyzed halogenation of methyl ketones leads to a haloform reaction,<sup>1-4</sup> and no intermediates can be isolated in this case; see Scheme 2.

It was suggested by Hughes *et al.*<sup>6</sup> and Watson *et al.*<sup>7</sup> that the halogenation of haloketones in acetic acid takes part mainly by a basic mechanism. Addi-

\* The papers in *Arkiv Kemi* 21 (1963) 503 and 24 (1965) 321 are regarded as Parts I and II, respectively, in this series.



SCHEME 2

tional proof for the basic mechanism has recently been obtained by the NMR study of the deuteration of haloketones in a medium prepared from acetic anhydride and  $\text{D}_2\text{O}$ . Small amounts of deuterium chloride diminished the rate of deuteration while sodium acetate increased it strongly.<sup>8</sup>

The kinetics of the base-catalyzed halogenation of acetone in acetate buffer solutions have recently been studied by Bell and Lidwell<sup>9</sup> and Bell and Yates.<sup>10</sup> Bell and Lidwell found that the ratio of halogenation for acetone, monochloroacetone and 1,1-dichloroacetone are approximately in the ratio 1:400:3000.<sup>9</sup> Therefore they assumed that the second and third stages of halogenation were very fast as compared with the first. They also assumed that substitution in a methyl group occurs more readily than in methylene or methine groups.<sup>9</sup> However, they did not isolate any products from their reactions. On the other hand, Schellenberger and Hübner,<sup>11</sup> who used radioactive iodine in the halogenation (followed by a haloform reaction), found that the acetate catalyzed iodination of butanone-2 yielded *only* monosubstituted derivatives. 3-Iodo- (Ic) and 1-iodobutanone-2 (IIc) were obtained in a ratio of I/II = 0.37 but the authors do not discuss this point.

Dubois and Barbier have studied the kinetics of the bromination of ketones in water in the absence of acid.<sup>12</sup> They assumed that in this medium, the enol was formed by an acid catalyzed reaction.

Here it can be pointed out that the brominations carried out by Cardwell and Kilner using potassium chlorate<sup>5</sup> are often referred to as typical examples of acid catalyzed brominations.<sup>13,14</sup>

In this communication we wish to report that the products obtained in the acetate and bicarbonate catalyzed bromination of butanone-2 or bromo derivatives of this ketone have been studied by NMR. The experiments were performed in four media:

- A. a solution of sodium acetate in acetic acid. Sodium halides separated out during the reaction.
- B. a solution of sodium acetate in acetic acid and water (1:1). (In reactions where 0.5 and 1.0 equiv. of bromine were used the bromoketones partly separated as heavy oils during the reaction).
- C. a two phase system of aqueous sodium acetate and ketone (and/or bromoketone).
- D. a two phase system of aqueous sodium bicarbonate and ketone (and/or bromoketone).

Sufficient base was added to ensure a base catalyzed reaction throughout the syntheses and the pH was checked after the bromine colour had dis-

appeared (pH = 5–7). In order to avoid polyhalogenation the experiments were performed with 0.125, 0.25, 0.50, and 1.0 equiv. of bromine.

In experiments performed according to methods A and B, water was added after the bromine colour had disappeared (2–100 h); and 1–2 ml of carbon tetrachloride subsequently added to achieve better separation. The heavy oil, which separated, was analyzed by NMR. A typical NMR-spectrum of this mixture of reaction products is given in Fig. 1. By comparison with

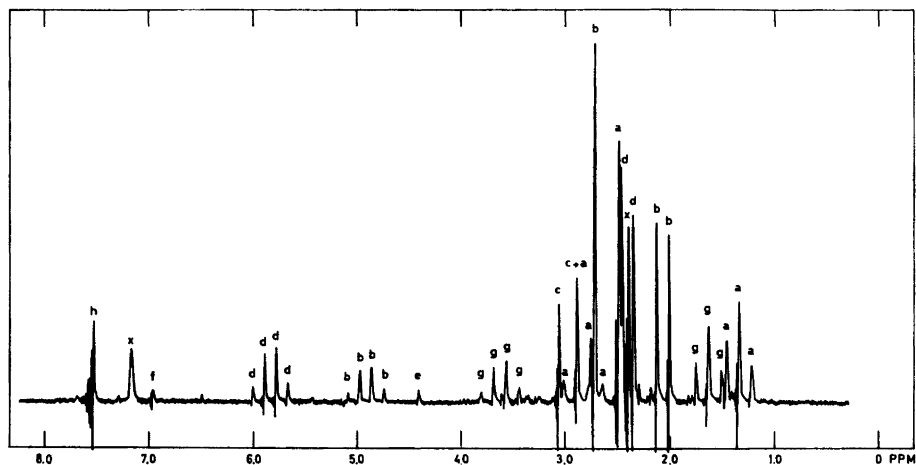


Fig. 1. NMR-spectrum of products from acetate catalyzed bromination of butanone-2.

NMR-spectra of known bromoketones, all the peaks were interpreted, as shown in Fig. 1. In addition to the starting material, butanone-2, *a*, the products are *b* = 3-bromo-; *c* = 3,3-dibromo-; *d* = 1,1,1,3-tetrabromo-; *e* = 1-bromo-; *f* = 1,1-dibromo-; *g* = 1,1,1-tribromobutanone-2 and *h* = bromoform (*x* = acetic acid). The results from the different experiments are collected in Table 1.

Unlike mono- and polyhaloketones, butanone-2 is soluble in water or dilute acetic acid. Therefore it is not possible to determine the proportion of this compound in the way used in this work. The proportion of only the haloketones and haloforms is given in Table 1.

Fischer *et al.*<sup>15</sup> found that bromine reacted slowly with a solution of sodium acetate in acetic acid. Blind tests were performed by the dropwise addition of bromine. Small amounts were decolorized and evolution of gas observed. However, after three weeks the colour of a solution of 0.25 equiv. of bromine in the amount of solvent used in the experiments still persisted. The mixture was analyzed by NMR, but no new peaks could be observed.

The bromine migration of the kind previously studied in acid media,<sup>16,17</sup> has not been observed in neutral or basic media. To obviate the possibility of such reactions, the chlorination of butanone-2 was studied, and the results are collected in Table 1 (expts. 20–23). The amount of chlorine used in these experiments was not estimated.

Table I. Results of the halogenation experiments.

Expt. No.	Ketone	Amount halogen	Method	b %	c %	d %	e %	f %	g %	h %	b+e %	KBr	Remarks
1	CH <sub>3</sub> CH <sub>2</sub> COCH <sub>3</sub>	0.125 Br <sub>2</sub>	A	46	6	14	9	8	17	—	55	1.6	2 % of (i)
2	»	0.25 Br <sub>2</sub>	A	37	5	29	5	2	19	1	42	1.8	
3	»	0.50 Br <sub>2</sub>	A	29	7	36	3	4	21	—	32	(1.5)	
4	»	1.0 Br <sub>2</sub>	A	10	6	47	3	2	29	1	13	(1.0)	2 % of (i)
5	»	0.125 Br <sub>2</sub>	B	47	—	7	8	3	21	14	55	1.5	
6	»	0.25 Br <sub>2</sub>	B	37	5	21	4	1	21	11	41	1.7	
7	»	0.50 Br <sub>2</sub>	B	33	6	27	3	1	16	15	36	(2.0)	
8	»	1.0 Br <sub>2</sub>	B	19	5	43	1	1	14	17	20	(1.7)	
9	»	0.125 Br <sub>2</sub>	C	74	6	—	6	3	5	6	80	4.8	
10	»	0.25 Br <sub>2</sub>	C	71	4	2	6	3	6	8	77	4.8	
11	»	0.50 Br <sub>2</sub>	C	66	4	6	9	4	4	7	75	3.8	
12	»	1.0 Br <sub>2</sub>	C	45	10	26	2	3	9	5	47	(3.1)	
13	»	0.125 Br <sub>2</sub>	D	76	12	—	4	2	6	—	80	7.3	2 % of (i)
14	»	0.25 Br <sub>2</sub>	D	63	22	1	2	1	7	2	65	6.7	
15	»	0.50 Br <sub>2</sub>	D	48	32	2	2	1	10	5	50	5.6	
16	»	1.0 Br <sub>2</sub>	D	50	12	1	1	2	14	20	51	(3.2)	
17	»	0.50 Br <sub>2</sub>	D	44	31	1	1	1	8	11	46	5.6	1 % of (i)
18	»	1.0 Br <sub>2</sub>	D	39	9	2	2	1	12	34	41	(2.7)	1 % of (i)
19	»	1.5 Br <sub>2</sub>	D	33	40	3	—	—	11	13	33	5.3	
20	»	Cl <sub>2</sub>	A	32	10	25	5	9	19	—	37	1.4	*
21	»	Cl <sub>2</sub>	B	33	5	26	4	4	18	10	37	1.6	*
22	»	Cl <sub>2</sub>	C	82	—	—	16	—	—	—	98	5.3	* 2 % of (j)
23	»	Cl <sub>2</sub>	D	84	—	—	15	—	—	—	99	5.6	* 1 % of (j)
24	CH <sub>3</sub> CHBrCOCH <sub>3</sub>	1.0 Br <sub>2</sub>	A	35	35	27	—	—	—	—	—	—	3 % of (i), 11 % of (k)
25	»	1.0 Br <sub>2</sub>	B	42	27	19	—	—	—	—	—	—	
26	»	1.0 Br <sub>2</sub>	C	44	29	9	—	—	—	—	—	—	
27	»	1.0 Br <sub>2</sub>	D	55	35	2	—	—	—	—	—	—	
28	CH <sub>3</sub> CH <sub>2</sub> COCH <sub>2</sub> Br	1.0 Br <sub>2</sub>	A	—	—	11	26	29	34	8	—	—	4 % of (i)
29	»	1.0 Br <sub>2</sub>	B	—	—	11	40	17	32	—	—	—	3 % of (i)
30	»	1.0 Br <sub>2</sub>	C	—	—	8	55	23	9	1	—	—	
31	»	1.0 Br <sub>2</sub>	D	—	—	1	52	27	16	1	—	—	

i = other polybromo ketones

j = 1,3-dichlorobutanone-2

k = 3-acetoxybutanone-2

In the present investigation two questions were of special interest: 1. the degree of halogenation, *i.e.* monohalogenation *versus* polyhalogenation, 2. the direction of halogenation, *i.e.* halogenation in the methylene group (3-halogenation) *versus* halogenation in the methyl group (1-halogenation).

As for the degree of halogenation, in reactions carried out in one-phase systems (methods A and B), polyhalogeno ketones were the main products — even when only 0.25 or 0.5 equiv. of bromine were added, while in those reactions performed in two-phase systems (methods C and D) monohalogenation was more pronounced. The amounts of monohaloketones are given in one column (b+e) of Table 1. Contrary to accepted theories the halogenation of butanone-2 in the presence of weak bases yielded large amounts of lower halogenated ketones.<sup>9,10</sup>

The difference between one- and two-phase systems may be explained by assuming that in two-phase systems the halogenation takes place in the aqueous phase. The solubility of unhalogenated ketones in this phase is appreciably greater than that of halogenated ketones — hence polyhalogenation is partly inhibited. This variance can also be explained on the basis of two different mechanisms — one in acetic acid/acetate buffer solutions and another in the more alkaline aqueous solutions of acetate and bicarbonate. This latter explanation is supported by the fact that polyhalogenation predominates in strongly alkaline solutions. It may be pointed out here that only very low amounts of haloforms could be detected in non-aqueous systems, see expts. 1–4 and 19.

In order to determine the direction of the halogenation it was desirable to ascertain which products are formed by a primary 3-halogenation and which by a primary 1-halogenation. The method of formation of two compounds is not clear, *viz.* 1,1,1,3-tetrahalobutanone-2 and haloforms.

Haloforms (V) are formed in the alkaline fission of 1,1,1-trihalo ketones (III); see Scheme 2. Determination of the acidic components (IV) formed in the same fission from expt. 10 showed that in addition to 3-acetoxybutanone-2, they contained 2-bromo- and 2,2-dibromopropionic acid (ratio 3/2), but no propionic acid. Under these experimental conditions only 1,1,1,3-tetrabromo- and 1,1,1,3,3-pentabromobutanone-2 were cleaved by the acetate, but not the 1,1,1-tribromo isomer. The acidic components in expt. 18, where the stronger base bicarbonate, was used, contained propionic acid as well as the bromosubstituted acids. Here it may be noted that 3-acetoxybutanone-2 was also detected among the ketonic components in expt. 26.

1-Bromo- and 3-bromobutanone-2 were brominated with 1.0 equiv. of bromine. The amounts of 1,1,1,3-tetrabromobutanone-2 (d) and bromoform (h) were higher in the case of the 3-bromo isomer, but the formation of these products from the bromination of the 1-bromo isomer cannot be neglected, see expts. 24–31, Table 1.

In order to calculate a ratio of amounts of products formed from a primary 3- and 1-halogenation, the approximation was made that two thirds each of the 1,1,1,3-tetrahalo ketones and of the haloforms were formed from a primary 3-halogenation and one third from a primary 1-halogenation. Then the ratio,  $K_{Br} = I/II =$  amounts of products from 3-halogenation/amounts of products from 1-halogenation, is given for the different cases in Table 1. It is clear that the most accurate determinations of this ratio were made in the

experiments where the proportions of 1,1,1,3-tetrahalo ketone and haloform were low. Therefore, the values of  $K_{Br}$  calculated from experiments with large amounts of these compounds are given within brackets in Table 1.

Like the degree of halogenation, the direction of reaction takes place in an unexpected way in the case of butanone-2 in the media under study. Although there is a difference here again between methods A and B, where the solvent is acetic acid, and the aqueous systems C and D, the ratio  $K_{Br}$  is throughout greater than 1.5 in the experiments where the amounts of 1,1,1,3-tetrabromobutanone-2 and bromoform are not too high. This means that the primary bromination of butanone-2 in acetate buffer, aqueous sodium acetate, and aqueous sodium bicarbonate catalyzed reactions takes place predominantly in the methylene rather than in the methyl group.

In methods A and B the  $K_{Br}$ -value was found to be 1.5–2 for bromination as well as chlorination experiments, while in methods C and D,  $K_{Br}$  was found to be 5–7. This indicates that in the more alkaline media the selectivity of the halogen for the methylene group is greater. In aqueous solutions of strong bases, it is the methyl group which is exclusively halogenated.<sup>1-4</sup> Therefore, changes in the pH of the solution cause differences in both degree and direction of halogenation.

Thus the halogenation of ketones seems to take place by three different mechanisms.

1. Acid catalyzed reactions; ( $K_{Br} > 1$ ).
2. Weak and moderate base catalyzed reactions; ( $K_{Br} > 1$ ).
3. Strong base catalyzed reactions; ( $K_{Br} \ll 1$ ).

Under usual experimental conditions, reaction 1, the halogenation of ketones in acid solutions, is known to be kinetically zero order in halogen. It has recently been found by Bell and Yates that the rate of halogenation is identical for all three halogens.<sup>10</sup> As proposed by Lapworth<sup>18</sup> the rate-determining step is the acid catalyzed enolization of the ketone; this is followed by rapid halogenation by  $X_2$  or  $X_3^\ominus$  of the enol. Yates and Wright have recently found that in this reaction, a halogenated carbonium ion, not a cyclic bromonium ion, is formed as an intermediate.<sup>19</sup>

Reaction 2 is generally accepted as halogenation of the enol formed in a base catalyzed enolization or the halogenation of the enolate anion.<sup>10,20-22</sup> Bell states that the pH of the solution determines which of these two routes is followed.<sup>20</sup> For 2-ethoxycarbonylcyclohexanone Bell and Vogelsong found that at pH = 5 both routes play an equal part.<sup>21</sup> For the bromination of ethyl malonate, Bell and Spiro found that at pH > 3 most of the bromination takes place through the anion, while below pH 3 bromination of the enol becomes more important.<sup>23</sup>

According to Table 1 differences in both the direction and the degree of halogenation were observed in the weak base catalyzed halogenation of ordinary ketones when the solution was changed from acetic acid/acetate solutions to aqueous acetate or bicarbonate, *i.e.* when the pH of the solution was changed. These differences indicate two alternative mechanisms and may perhaps be explained in the following way.

Although the halogenation of halo ketones in acetic acid/acetate solutions is a base catalyzed reaction, *the halogenation of an unsubstituted ketone in this solvent can still be an acid catalyzed reaction*. The ratio  $K_{Br}$  in this investigation is about the same as found by Cardwell *et al.*<sup>5</sup> for the strong acid catalyzed halogenation of the same ketone. In this connection it can be pointed out that the halogenation of 1,1,3-tribromoacetone at  $pH = 0$  (2 N hydrochloric acid) was found to be a base catalyzed reaction, while at  $pH = 2.5$  the halogenation of monochloroacetone was found to be an acid catalyzed reaction.<sup>6-8</sup>

The halogenation in aqueous acetate and bicarbonate would be a base catalyzed reaction, and the mechanism for this reaction is considered to be the halogenation of the enol. *This halogenation takes place predominantly in the methylene group and not in the methyl group in disagreement with accepted theories.*<sup>1-4,9,10</sup>

Some of the experiments with bicarbonate gave much higher amounts of bromoform and much lower amounts of 3,3-dibromobutanone-2, the other components being unchanged; see expts. 16 and 18, Table 1. This indicates an alkaline fission of 3,3-dibromobutanone-2 in these experiments. The reason for this fission is still unclear. Additional support for this view was obtained by analyzing the acidic components in these experiments. The amount of 2,2-dibromopropionic acid was found to be higher.

In this paper, only the problems concerning the introduction of the first halogen in the ketone molecule are discussed. The weak base catalyzed halogenation of halo ketones will be submitted to more experimental work and discussed elsewhere.

Turning to reaction 3, the halogenation in strong alkaline solutions — as the products in this reaction are different from those in the acetate and bicarbonate catalyzed reactions, reaction 2, these two reactions take place by different mechanisms. It is likely that the reaction in strong alkaline solutions is the halogenation of the enolate anion. The halogenating species can be hypohalous acids, which can react directly with the enolate, as suggested by Cullis and Hashmi for iodinations and brominations in strong alkaline solutions.<sup>24-26</sup> Another possibility is suggested by Hulett, the hypohalite ions being the halogenating species.<sup>27</sup> Here it can be noted that among the acid components Cullis and Hashmi found both unbrominated acids and  $\alpha$ -monobromo acids but no  $\alpha,\alpha$ -dibromo acids.<sup>24-26</sup>

In order to clarify the complex situation more experimental work is being carried out. This will include the halogenation of a variety of ketones under different conditions. Of special interest would be ketones of known, high enol content. From these experiments the ketonic as well as the acidic products will be analyzed. In addition, the weak base catalyzed halogenation of ketones will be tried on a preparative scale. The rates of halogenation, using different halogens, will be compared with each other as well as with the rate of deuteration. Theoretical aspects of the different mechanisms for halogenation will be discussed.

Table 2. Experimental conditions.

Expt. No.	Ketone	Amount g	Solvent	Base	Amount g	Time for decolorizing h	Amount water added ml
1	CH <sub>3</sub> CH <sub>2</sub> COCH <sub>3</sub>	14.4	30 ml of HOAc	NaOAc	5	20	150
2	»	7.2	»	»	5	48	150
3	»	3.6	»	»	5	72	150
4	»	3.6	50 ml of HOAc	»	10	96	250
5	»	14.4	20 ml of H <sub>2</sub> O + HOAc(1:1)	»	5	8	100
6	»	7.2	»	»	5	14	100
7	»	3.6	»	»	5	24	100
8	»	3.6	40 ml »	»	10	30	100
9	»	14.4	20 ml of H <sub>2</sub> O	»	5	20	—
10	»	7.2	»	»	5	36	—
11	»	3.6	»	»	5	50	—
12	»	3.6	30 ml of H <sub>2</sub> O	»	10	72	—
13	»	14.4	70 ml of H <sub>2</sub> O	NaHCO <sub>3</sub>	5	2	—
14	»	7.2	»	»	5	3	—
15	»	3.6	»	»	5	7	—
16	»	3.6	»	»	5	4	—
17	»	3.6	120 ml of H <sub>2</sub> O	»	10	15	—
18	»	3.6	»	»	10	5	—
19	»	3.6	»	»	15	24	—
20	»	18.0	100 ml of HOAc	NaOAc	15	10	50 <sup>a</sup>
21	»	18.0	60 ml of H <sub>2</sub> O + HOAc(1:1)	»	15	5	50 <sup>a</sup>
22	»	18.0	50 ml of H <sub>2</sub> O	»	15	5	—
23	»	18.0	150 ml of H <sub>2</sub> O	NaHCO <sub>3</sub>	15	5	—
24	CH <sub>3</sub> CHBrCOCH <sub>3</sub>	3.0	30 ml of HOAc	NaOAc	5	2	—
25	»	3.0	12 ml of H <sub>2</sub> O + HOAc(1:1)	»	5	12	150
26	»	3.0	10 ml of H <sub>2</sub> O	»	5	8	100
27	»	3.0	70 ml of H <sub>2</sub> O	»	5	20	—
28	CH <sub>3</sub> CH <sub>2</sub> COCH <sub>2</sub> Br	3.0	30 ml of HOAc	NaHCO <sub>3</sub>	5	12	—
29	»	3.0	12 ml of H <sub>2</sub> O + HOAc(1:1)	NaOAc	5	1	150
30	»	3.0	10 ml of H <sub>2</sub> O	»	5	2	100
31	»	3.0	70 ml of H <sub>2</sub> O	NaHCO <sub>3</sub>	5	1	—

<sup>a</sup> = To a sample of 10 ml of the solution.



## EXPERIMENTAL

The NMR-spectra were recorded on a Varian model A-60 spectrometer.

*3-Bromobutanone-2* was prepared according to Rappe and Kumar,<sup>28</sup> b.p. 30–32°C/9 mm,  $n_D^{25} = 1.4581$ .

*1-Bromobutanone-2* was prepared according to Catch *et al.*,<sup>29</sup> b.p. 46–48/11 mm,  $n_D^{25} = 1.4658$ .

*Halogenations.* Compositions in the different runs are given in Table 2. The mixture was thoroughly stirred and when the bromine colour had disappeared, see Table 2, water and carbon tetrachloride were added and the heavier organic layer analyzed by NMR. The composition of these samples is given in Table 1. The reaction mixture was extracted with carbon tetrachloride (5 ml), acidified and re-extracted with ether, the ether evaporated and the residue was analyzed by NMR.

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