thetic 3β,28-diacetoxy-lupan-20-ol (see below). (Found: C 75.5; H 10.1; O 14.5. Calc. for $C_{34}H_{56}O_5$: C 75.0; H 10.4; O 14.7).

The mass spectra of compound *B*, synthetic 3β,28-diacetoxy-lupan-20-ol and betulinol diacetate were identical. No peak was observed for the molecular ion of 3β,28-diacetoxy-lupan-20-ol (below called M^+). Some of the peaks were: *m/e* 526 (M^+ minus H_2O) (15 % of the base peak), 511 (the base peak), 453 (11 %), 423 (14 %), 249 (the *g* fragment [9]) (8 %), and 189 (58 %).

Synthesis of 3β,28-diacetoxy-lupan-20-ol. 3β,28-Diacetoxy-20,29-epoxy-lupan [10] (1.0 g, m.p. 200–217°C) was reduced with lithium aluminium hydride as described for the synthesis of lupan-3β,20-diol from the corresponding epoxide.[4] The reduced material was acetylated with pyridine and acetic anhydride at room temperature. The product (0.58 g) was purified by TLC (silica gel, 1 % methanol in isopropyl ether) and recrystallisations from acetonitrile and hexane: m.p. 253–256°C, $[\alpha]_{578}$ + 4° (*c* 0.5, $CHCl_3$) (0.10 g, yield 10 %). (Found: C 75.0; H 10.4. Calc. for $C_{34}H_{56}O_5$: C 75.0; H 10.4).

Its proton magnetic resonance spectrum agreed with the structure (V) (*cf.* Ref. 11): δ 0.85 ppm (strong singlet), 4α, 4β and 10-CH_3: δ 1.03 ppm (singlet), 14-CH_3: 1.10 ppm (singlet), 8-CH_3: δ 1.15 and 1.25 ppm (two singlets), 21- and 22-CH_3: δ 3.90 and 4.44 ppm (two doublets, $J_C = 11$ cps), 28-H: δ 4.57 ppm (triplet, $J_C = 7$ cps), 3α-H.

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Halogenation of Ketones

V.* Studies on the Mechanisms of Base Catalyzed Halogenations of Butanone-2

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In 1904 it was proposed by Lapworth that the rate determining step in the acid catalyzed halogenation of ketones is the enolization of the ketone.[1] Later, the same author proposed the same step as being rate determining in the base catalyzed reaction.[2] In 1932 Watson and Yates proposed that the base catalyzed halogenation of ketones involves both the enolate anion and the enol.[3] The currently accepted view is that halogenation of ketones can proceed by either an acid or a base catalyzed reaction, the enolization or formation of the enolate anion being the rate determining step in both cases.[4-10]

In a recent paper the present author gave the first experimental evidence for *two* different mechanisms for the base catalyzed halogenation of ketones.[11] In that paper the sodium acetate and sodium bicarbonate catalyzed chlorination and bromination of butanone-2 were studied. The products were analyzed by NMR and the value of the ratio 3-halogenation/1-halogenation (K_{Hal}-values) were determined. In these weak base catalyzed reactions these values

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were found to be different from those obtained in the hydroxide catalyzed halogenation.[11]

In the present communication we wish to report that this work has been much extended. Other bases and other concentrations of the bases have been used. In some experiments the products from the base catalyzed iodination have been studied.

A brief comparison of the reaction rates of base catalyzed bromination and iodination has been made. In halogenations performed in D_2O the rate of halogenation has been compared with the rate of deuteration. The rate of deuteration in these reactions has also been compared with the rate of deuteration in reactions without any added halogen. The products from the reaction between hypobromous acid and butanone-2 using various catalysts has also been studied.

All this work supports the hypothesis that two different mechanisms can operate in the base catalyzed halogenation of ketones. In this paper these reactions are called Hal B I and Hal B II. From the experiments and a comparison of these with the deuterations of butanone-2 using the same bases,[12] it appears that the currently accepted mechanism for the base catalyzed halogenation of ketones is not valid in either of the two halogenations.

In reaction Hal B I, which takes place in neutral and in moderately acidic and alkaline solutions, both halogens and hypohalous acids can be used as the halogenating reagent. The reaction has a pronounced tendency for 3-halogenation, $K_{\mathrm{Hal}} = 6.5-7$. It seems to be a reaction between the unenolized ketone, hypohalous acid and the base, but the exact nature of the reaction is still not clear. At least two mechanisms can be discussed. The reaction can either be a concerted process, where the attack of hypohalous acid on the unenolized ketone is catalyzed by the weak base, or an attack on the ketone by a product of hypohalous acid and another halogenated component formed in a base catalyzed reaction of hypohalous acid. The experimental data for the weak base catalyzed halogenation, which have led to this hypothesis are:

1. The observation of two different base catalyzed halogenations.
2. In the weak base catalyzed reactions the values of 3-halogenation/1-halogenation (K_{Hal}) are different from the values of 3-deuteration/1-deuteration (K_{D}).
3. Difference in the reaction rate for bromine and iodine.
4. The reactions are performed at pH $5-7$.
5. In a D_2O/base solution the rate of deuteration is not influenced by the addition of bromine.
6. A positive catalytic effect by sodium acetate.
7. Negative catalysis by sodium bromide, positive by sodium chloride.
8. Slow reaction of the ketone with only hypobromous acid.
9. A fast reaction with ketone, hypobromous acid, and sodium acetate.
10. Positive catalysis by halides on this reaction.
11. The same K_{Hal}-value of the product from this reaction as from the acetate catalyzed halogenation.

In the other base catalyzed halogenation, reaction Hal B II, which operates in strongly alkaline solutions, the tendency for 1-halogenation is great in the case of butanone-2 ($K_{\mathrm{Hal}} = 0$). In this case, a mechanism involving hypohalite ions and the unenolized ketone is proposed, and the experimental data, which indicate this mechanism are:

1. The observation of two different base catalyzed halogenations.
2. In strong base catalyzed reactions the K_{Hal}-values are different from the K_{D}-values.
3. The reactions are performed at pH $12-14$.
4. In a D_2O/base solution no deuteration occurs during the time bromination goes to completion.
5. The same result with normal and reverse addition of the components.
6. More than one equivalent of base is without influence on the reaction rate.

A more detailed account of this work is being prepared.

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On the Nature of Charge-carriers in Liquid Se Containing Cl

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The conductivity of liquid selenium is considerably increased by addition of small amounts of chlorine. It was recently pointed out by us [1] that it might be advantageous to apply a "chemical" approach for finding the nature of the charge-carriers. From studies of the conductivity of a melt at equilibrium with $SeCl_2$(g) at various partial pressures $p(SeCl_2)$, it should be possible to apply the law of mass action and conclude how many charged particles are formed for each $SeCl_2$.

The preliminary experiments, reported in that paper, seem to indicate that the increase in conductance, $\varkappa - \varkappa_0$, is proportional to the square root (power 1/2) of $p(SeCl_2)$, which would indicate that only two charged particles are formed per $SeCl_2$ dissolved. Several possible mechanisms were suggested.

In the meantime, however, we have made more accurate measurements and especially have been able to use electrodes and cell materials that are less attacked by the melt than those used earlier. This has led us to a modification of our conclusions.

Cell material. All experiments described here were carried out on Se(l) at 280°C. The first cells were made of soda glass, for practical convenience, but it was found that they gave a higher value for the conductivity of pure Se, $\varkappa_0$, than cells of quartz glass. So, in the following, quartz was used in the cells.

Electrode material. At first Pt electrodes were used. However, they were slowly attacked by the melt, and other electrode materials were thus tried. With wolfram electrodes, $\log \varkappa_0 = -6.70 \pm 0.05$ was found, to be compared with -6.55 ± 0.05 for Pt electrodes. This might indicate that W interacts less with the melt than Pt; we found no evidence for a surface resistance. Unfortunately, the W electrodes did not work well when the melt was equilibrated with $SeCl_2$(g): only irreproducible data were obtained which indicates that there is a reaction between W and Cl in these surroundings.

During the Se Symposium in London, 1964,[1] we learnt about the availability of a vitreous form of carbon [2] which we then tried as an electrode material. We found with vitreous carbon electrodes the same low value, $\log \varkappa_0 = -6.70 \pm 0.05$, as with the W electrodes, and moreover, there was

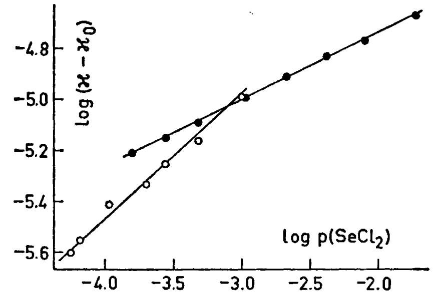

Fig. 1. Conductivity of liquid Se at equilibrium with $SeCl_2$(g) of various partial pressures: $\log (\varkappa - \varkappa_0)$ as a function of $\log p(SeCl_2)$. Open circles show earlier experiments with a soda glass cell with Pt electrodes. Filled circles show one series of experiments in a quartz cell with vitreous carbon electrodes. Other series give lines of the same slope but may be shifted parallelly by $\pm$ 0.07 units in $\log (\varkappa - \varkappa_0)$.