

the samples on the other side of the eutectic, *i.e.* with less than 55% CaF_2 , the formation of glass is first preceded by a precipitation of TiO_2 . As a consequence the composition of the melt is, *e.g.*, changing from A_1 to C_1 or from A_2 to C_2 according to Fig. 2. When the composition of the melt has reached the boundary between the crystallization fields for TiO_2 and CaF_2 , the precipitation continues along that boundary while the two phases TiO_2 and CaF_2 are crystallizing simultaneously. The glass formed in samples to the left of the eutectic may thus have the same composition as the glass formed in samples to the right of the eutectic and the exact composition of this glass is not necessarily depending on the initial composition of the melted sample.

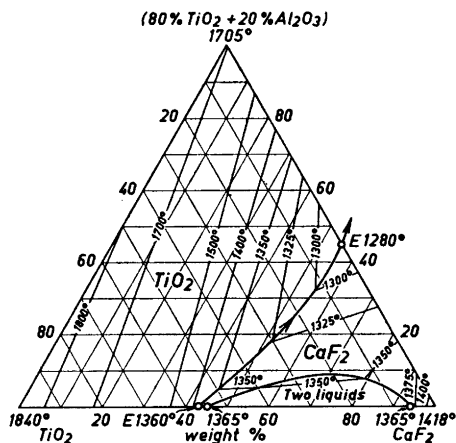


Fig. 3. Tentative phase diagram for the system TiO_2 -(80% TiO_2 + 20% Al_2O_3)- CaF_2 . TiO_2 -(80% TiO_2 + 20% Al_2O_3) according to Ref. 8; TiO_2 - CaF_2 according to Ref. 1; (80% TiO_2 + 20% Al_2O_3)- CaF_2 according to this investigation.

In combining the results of the present work with those of Refs. 1 and 8 an attempt has been made to construct the ternary phase diagram for the system TiO_2 -(80% TiO_2 + 20% Al_2O_3)- CaF_2 (Fig. 3). Nothing is known about the extension of the two-liquid area of the system TiO_2 - CaF_2 into the ternary system. Thus its extension was drawn tentatively in Fig. 3. The ternary phase diagram TiO_2 -(80% TiO_2 + 20% Al_2O_3)- CaF_2 in Fig. 3 shows the

boundary between the primary crystallization fields for TiO_2 and CaF_2 and the liquidus isotherms.

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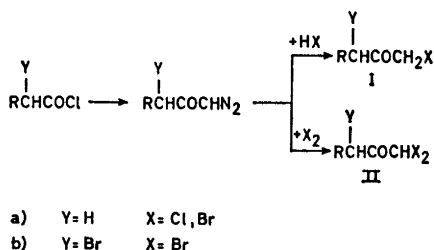
The Preparation of 1,1-Dichloro-3,3-dibromobutanone-2

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In connection with work on the mechanism of the Favorsky rearrangement, we wished to prepare 1,1-dichloro-3,3-dibromobutanone-2.¹ The common method for the preparation of tetrahaloketones is the acid catalyzed halogenation.² However, in the present case, this method seems to be without success. Although 3,3-dibromobutanone-2 can be prepared in good yields by bromination with *N*-bromosuccinimide,³ it rearranges easily in acid media to the symmetrical 1,3-dibromobutanone-2.⁴

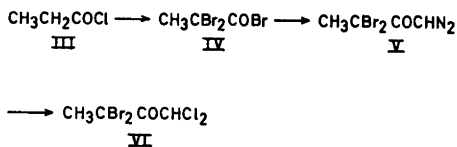
The Arndt-Eistert synthesis has shown itself to be useful in the preparation of certain α -haloketones. α -Monohaloketones, Ia, Scheme 1, can be prepared in good yields from diazoketones and hydrohalic acids.⁵ By the use of α -monobromosubstituted acid chlorides it was possible to prepare α,α' -dibromoketones, Ib.⁶



SCHEME 1

If the diazoketone or the monobrominated diazoketone were treated with free bromine instead of hydrobromic acid, α,α -dibromo- (IIa) or α,α,α' -tribromoketones (IIb) could be prepared.^{4,7} Because of secondary rearrangements these ketones could not be prepared in a pure state.^{4,7} In one example a tribromoketone was prepared from an α,α -dibromosubstituted acid chloride.⁸

In the present synthesis we tried the reaction between an α,α -dibromodiazoketone and chlorine, see Scheme 2.



SCHEME 2

As starting material we needed an acid halide of 2,2-dibromopropionic acid, but no acid halide of this compound seems to have been described in literature.

2,2-Dibromopropionyl bromide, IV, Scheme 2, can be prepared in good yields by the bromination of propionyl chloride, III, under illumination. Elementary analyses indicated that it was exclusively the acid bromide and not the acid chloride which was formed in this reaction. The

diazoketone, V, prepared in the usual way, was treated with the calculated amount of chlorine, dissolved in carbon tetrachloride.

NMR-analyses of the crude product showed that only about 65% consisted of the expected tetrahaloketone (VI) and distillation of the crude product did not improve the purity. When the reaction product was left at 0°C for a week, the tetrahaloketone (VI) crystallized out and could be separated. Recrystallization gave the wanted compound in a pure state.

NMR-spectra indicated that the impurity was a trihaloketone, probably 1-chloro-3,3-dibromobutanone-2. Now the question arises how this compound can be formed.

This synthesis seems to be the first where chlorine was used in an Arndt-Eistert synthesis. In order to get more information about the reaction between a diazoketone and chlorine, we tried to prepare 1,1-dichloroheptanone-2 in an analogous way, starting from caproyl chloride. However, although the excess of diazomethane was high, a monochloroketone was the main product in this case. A number of other impurities was also found, and the percentage of the wanted 1,1-dichloroketone was only about 30%. 1-Chloroheptanone-2 was prepared in an ordinary Arndt-Eistert reaction using hydrogen chloride, and a comparison of the NMR-spectra showed that the two compounds were identical.

An explanation of this unexpected behaviour where a monochloroketone was the result, although chlorine was used in the synthesis, seems to be that unlike bromine, chlorine reacts faster with the solvent ether in a substitution reaction than with the diazoketone. In this substitution reaction, hydrogen chloride is a product, and this hydrogen chloride reacts with the diazoketone to give a monochloroketone, Ia; see Scheme 1. A synthesis was performed where most of the ether was evaporated and exchanged for carbon tetrachloride before the addition of chlorine. In this case 1,1-dichloroheptanone-2 was the main product, purity 80% of the crude product (NMR), the rest being monochloroketone.

Work is in progress to find a better solvent for the syntheses and to study the stability of the diazoketones, halogenated as well as unhalogenated. The present investigation seems to indicate that the halogenated diazoketones are sometimes more reactive than unhalogenated diazoketones.

Experimental. 2,2-Dibromopropionyl bromide (IV). To 92.5 g (1.0 mole) of boiling propionyl chloride (III) and 1.0 g of red phosphorus, bromine was added over a period of 60 h. The reaction vessel was illuminated with a 500 W bulb. When the bromine colour persisted, nearly 2.0 moles (320 g) having been consumed, the product was distilled. From the distillation 207 g (70 %) of 2,2-dibromopropionyl bromide (IV) was collected, b.p. 70°C at 10 mm Hg. (Found: C 11.84; H 1.00; Br 80.95. Calc. for $C_3H_5Br_2O$: C 12.22; H 1.03; Br 81.32).

1,1-Dichloro-3,3-dibromobutanone-2 (VI). To 21.0 g (0.5 mole) of diazomethane, prepared according to Ref. 9 and dissolved in 1000 ml of dry ether was added 44.3 g (0.15 mole) of 2,2-dibromopropionyl bromide (IV) dissolved in 100 ml of dry ether and kept at 0°C. After 2 h the excess of diazomethane was distilled. Chlorine dissolved in carbon tetrachloride at 0°C was added until nitrogen evolution ceased. The reaction product was washed with water until the washings were almost neutral, the ethereal phase dried with magnesium sulphate and the ether evaporated, the last traces *in vacuo*. The crude product was left at 0°C for a week for crystallization and the crystals collected, 9.0 g (20 %), m.p. 45–50°C. Crystallization from ethanol raised the m.p. to 51–51.5°C. (Found: C 16.09; H 1.41. Calc. for $C_4H_4Br_2Cl_2O$: C 16.08; H 1.35).

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On the Phase Diagram Barium Chloride — Potassium Chloride

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The phase diagram $BaCl_2-KCl$ has been re-determined with a view to ascertaining the possible presence of complex ions in the liquid mixture. This diagram has a peak at around 33.3 mole% $BaCl_2$, indicating the presence of a congruently melting compound, K_2BaCl_4 .

The previously published phase diagrams of this system by Gemsky¹ and Elchardus and Lafitte² both exhibit the same general shape as the one obtained from this investigation. But as the latter diagrams are based on relatively few experimental results, the detailed shape of the compound peak is not unambiguously given. As shown by Grjotheim³ a detailed knowledge of the shape of the peak may provide valuable information as to the nature of the ionic species of the melt.

Compound formation is a general feature of many binary alkali-alkaline earth halide mixtures. A survey of the various bromide mixtures has been given by Kellner.⁴ The following compounds have been found to exist in the solid state: $LiSr_2Br_3$, $NaCa_2Br_3$, $KMgBr_3$, K_2MgBr_4 , $KCaBr_3$, K_2SrBr_4 , KSr_2Br_3 , K_2BaBr_4 . A correspondingly extensive study of the chloride mixtures has not been carried out, but the existence of the compounds $KCaCl_3$,⁵ K_2SrCl_4 , KSr_2Cl_3 ,⁶ and K_2BaCl_4 ,^{1,2} is well established.

No investigation of the structure of the binary compounds has been reported in the literature. At present, the structure of K_2BaCl_4 is being investigated by single-crystal X-ray diffraction methods at our Institute.

In the present investigation the phase diagram $BaCl_2-KCl$ has been determined by thermal analysis, the results of which is given in Table 1. The phase diagram is depicted in Figs. 1, 2, and 3. Fig. 1 also gives the agreement of the present results with earlier data. The compound K_2BaCl_4 has a congruent melting point of $661 \pm 0.5^\circ C$, and the eutectics at 658 and 648 ($\pm 0.2^\circ C$) contain 25.9 and 42.9 mole % $BaCl_2$, respectively. The high tem-