CCXCII.—*Bromine Chloride; the Action of Mixtures of Chlorine and Bromine on Aliphatic Diazo-Compounds.*

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OF recent years evidence is accumulating that, contrary to the older ideas, in a mixture of chlorine and bromine, either as gases or in solution, a considerable proportion of the halogens exists as bromine chloride, BrCl. Reference may be made to the electrometric work of Forbes and Fuoss (*J. Amer. Chem. Soc.*, 1927, **49**, 142), to the spectrophotometric work of Barratt and Stein (*Proc. Roy. Soc.*, 1928, *A*, **122**, 582) based on an observation of Dobson, and to the vapour pressure measurements of Lux (*Ber.*, 1930, **63**, 1156). On the chemical side, the work of Delépine and Ville (*Bull. Soc. chim.*, 1920, **27**, 673) on the addition of the mixed halogens to unsaturated compounds points in the same direction, but the objection might be raised that the possibly complicated mechanism of this reaction may obscure the issue.

Chlorine and bromine react very rapidly and energetically with aliphatic diazo-compounds, a molecule of nitrogen being expelled and a molecule of the halogen taking its place :

$$CRR'N_2 + Hal_2 \longrightarrow CRR'Hal_2 + N_2.$$

If bromine chloride is present to an appreciable extent in mixtures of bromine and chlorine, the product obtained by using the mixture in this reaction might be expected to consist of the chlorobromo-compound together with the dichloro- and the dibromo-compound. If, because of the great ease with which the reaction proceeds, it is assumed that there are no complicating factors present, the proportions in which the three products are formed will be a measure of the proportions of the molecules Cl_2, Br_2, and BrCl in the original mixture.

Ethyl diazoacetate was allowed to react with the equivalent of an equimolecular mixture of chlorine and bromine in carbon tetrachloride solution. The mixed dihalogen esters formed were fractionated under 30 mm. pressure. From the middle fraction (b. p. 80—85°), on treatment with concentrated aqueous ammonia, chlorobromoacetamide, identical in melting point and properties with specimens synthesised by two other different methods, was obtained. In order to make sure that the substance was not an equimolecular compound of dichloro- and dibromo-acetamides, the melting-point curve for mixtures of these substances was determined; these two amides form an unbroken series of solid solutions and the equimolecular mixture melts over a range of temperature, the temperature of complete fusion being 137°. The chlorobromoacetamide on the contrary melted sharply at 129·0°.

If the total esters from such an experiment are converted into amides and recrystallised several times, more than half the product consists of chlorobromoacetamide. This indicates that the equilibrium $Br_2 + Cl_2 \rightleftharpoons 2BrCl$ lies over to the right-hand side. The method using diazoacetic ester, however, is not suitable for obtaining quantitative results. It is very difficult to devise a method for estimating mixtures of dichloro-, dibromo-, and chlorobromo-acetic esters; and, though this could be done for the corresponding amides, the conversion of esters into amides is not quantitative, some halogen being lost during the process.

To overcome this difficulty benzoylphenyldiazomethane, $Ph{\cdot}CN_2{\cdot}COPh$, was taken as starting point, since the reaction products, dichloro-, dibromo-, and chlorobromo-deoxybenzoins, are all solids melting without decomposition. This diazo-compound was allowed to react with its equivalent of an equimolecular mixture of chlorine and bromine and an attempt was made to separate from the product chlorobromodeoxybenzoin in a state of purity. Alcohol proved useless as solvent, since the halogen atoms in the compounds reacted with it to a slight extent in hot solution and, as the crystallisations proceeded, the product became more and more contaminated with benzil. The use of light petroleum overcame this difficulty, but ten recrystallisations failed to give a pure product. The melting-point curves for binary and ternary mixtures of these three deoxybenzoins showed later that all form solid solutions with each other and the attempt was abandoned, though the melting points of the final fractions together with their bromine and chlorine content showed that chlorobromodeoxybenzoin was present in considerable quantity.

Chlorobromodeoxybenzoin was obtained by the bromination of monochlorodeoxybenzoin and the melting-point curve for mixtures of this substance with varying amounts of an equimolecular mixture of dichloro- and dibromo-deoxybenzoins was determined. Since the product of the reaction of the diazo-compound with an equimolecular mixture of chlorine and bromine must consist of equimolecular amounts of the dichloro- and dibromo-compounds together with the chlorobromo-compound, determination of its melting point and reference to this curve will give its composition.

In actual fact, however, this product is always contaminated with a small amount of a gummy material, the complete removal of which offers great difficulty; it is best accomplished by recrystallisation from ligroin, but this process upsets the constancy of the chlorine–bromine ratio to a small extent. The melting point of the product after this treatment varies between the limits 94° and 91°, so that as a mean result, which is not of a high degree of accuracy, the composition of the reaction product can be taken as 80 mols. % of chlorobromodeoxybenzoin and 10 mols. % of each of the dichloro- and dibromo-compounds. On the assumption made here, the same figures express the proportions of the molecules in the equilibrium $Br_2 + Cl_2 \rightleftharpoons 2BrCl$.

The only results with which this figure can be compared are those of Barratt and Stein (*loc. cit.*), who also used solutions in carbon tetrachloride. Their results vary widely, the mean being that roughly 50 molecules of bromine chloride are in equilibrium with 25 of each of chlorine and bromine. They worked, presumably, at room temperature, while our reaction mixture was always kept in a bath at 0°, but the reaction is vigorous and exothermic and accurate temperature control was impossible. The equilibrium, however, is probably very little affected by temperature, since there is no observable heat change on mixing solutions of the two halogens and, further, Dobson has found that the absorption spectrum of chlorine–bromine light filters does not alter appreciably with change of temperature. The divergence between our result and that of Barratt and Stein arises either because their assumption as to the absorption of bromine chloride in the visible part of the spectrum is not justified, or else because of the failure of our own assumption. If the absorption of bromine chloride extends further into the visible region than they assume, it is possible that the concentrations of free bromine measured by them are too great and the divergence between the two sets of results receives some explanation.

EXPERIMENTAL.

Throughout this work chlorine and bromine were used as solutions in purified carbon tetrachloride which had been standardised iodometrically. The estimations of the chlorine and bromine were carried out (a) with the acetamides, by boiling a weighed sample with concentrated potash solution, precipitating the mixed silver halides, weighing them, heating them in a stream of chlorine and weighing again (even the purest samples of potassium hydroxide contained enough chloride to interfere with this method; so the chloride content of a stock solution was estimated and, known amounts of this solution having been used, the necessary correction was applied); (b) with the deoxybenzoins, by boiling a weighed sample with alcoholic silver nitrate, filtering off the silver halides, and proceeding as before.

All temperatures given are corrected for the emergent stem.

Chlorobromoacetamide obtained from the reaction product melted at 129·0° (Found: Cl, 20·1; Br, 46·7. Calc.: Cl, 20·6; Br, 46·4%). The compound was also prepared from ethyl chlorobromomalonate (Conrad and Brückner, *Ber.*, 1891, **24**, 2995) and from ethyl chlorobromoacetoacetate (Conrad and Schmidt, *Ber.*, 1896, **29**, 1045). These authors give a melting point of 117°; our products, after several recrystallisations from benzene, melted at 129° (Found: C, 14·1; H, 1·7; N, 8·2; Cl, 20·7; Br, 46·4. Calc.: C, 13·9; H, 1·7; N, 8·1; Cl, 20·6; Br, 46·4%). These analyses agree with the calculated values better than do those of Conrad and Brückner and they were probably dealing with an impure specimen, unless, as with other amides, polymorphism occurs here.

When these samples were mixed with those from the reaction product, there was no depression of the melting point.

Dichloroacetamide was obtained by the action of aqueous ammonia on ethyl dichloroacetate: after recrystallisation from benzene it melted at 99·4°. Dibromoacetamide prepared similarly melted at 155·5°. The temperatures of complete fusion of binary mixtures of these two compounds which were determined were :—

Mols. % $CHBr_2{\cdot}CO{\cdot}NH_2$	13·8	27·2	46·95	65·6
Temperature	123·2°	128·4°	135·7°	143·8°

Benzoylphenyldiazomethane: contrary to the observations of Forster and Cardwell (J., 1913, **103**, 868), purified benzene was found to be a much better solvent than ether for the oxidation of benzilmonohydrazone. The solvent was removed at 30° under reduced pressure; the product, recrystallised from ligroin (b. p. 60—80°), melted at 81·8° (decomp.) (Staudinger and Gaule, *Ber.*, 1916, **49**, 1911, give 79°).

Dichloro- and dibromo-deoxybenzoins were obtained by the action of the halogens on benzoylphenyldiazomethane (Found: Cl, 26·5. Calc., 26·8%. Found: Br, 44·8. Calc., 45·2%). The temperatures of complete fusion of binary mixtures of these compounds observed were :—

Mols. % $Ph{\cdot}CBr_2{\cdot}COPh$	0	20·0	29·0	33·6	42·8
Temperature	60·0°	77·8°	85·2°	92·0°	94·0°
Mols. % $Ph{\cdot}CBr_2{\cdot}COPh$	54·7	66·2	79·5	92·1	100
Temperature	98·0°	104·5°	106·2°	111·0°	111·0°

Monochlorodeoxybenzoin (desyl chloride) was obtained from thionyl chloride and benzoin (Schroeter, *Ber.*, 1909, **42**, 2348); for the reaction to proceed satisfactorily a third more thionyl chloride than is recommended by Schroeter was found necessary. The initial product was a black viscous liquid which slowly solidified and from which the desired compound was obtained by extraction with warm ligroin (b. p. 60—80°); the solution was decanted from the oil which separated on cooling, and the product crystallised on further cooling in ice and salt. It was best recrystallised from light petroleum and melted at 65·5°.

Chlorobromodeoxybenzoin was prepared by the action of the theoretical amount of bromine on chlorodeoxybenzoin in glacial acetic acid solution; the reaction was complete after 30 minutes' heating on the steam-bath. The product crystallised in part on cooling or was obtained by pouring the mixture into water. It formed colourless prisms, m. p. 85° (after four recrystallisations from ligroin) (Found: Cl, 10·8, 11·2; Br, 26·0, 24·9. $C_{14}H_{10}OClBr$ requires Cl, 11·4; Br, 25·8%).

The temperatures of complete fusion of ternary mixtures of the dichloro-, dibromo-, and chlorobromo-compounds made up from an equimolecular mixture of the first two substances and varying amounts of the third were observed to be as follows :—

Mols. % Ph·CClBr·COPh ...	92·1	75·4	62·3	39·1	10·95	0
Temperature	88·4°	93·8°	95·2°	96·0°	96·4°	96·8°

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