CIII.—*Tribromophenol Bromide (Dibromobenzene Ketodibromide).*

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IN studying the action of bromine on the acid obtained by sulphonating anisic acid, a substance was obtained having the composition of tribromophenol bromide (dibromobenzene ketodibromide), but not all the properties ascribed to that compound, the substance obtained by me melting, when recrystallised from ethyl acetate, at 147—148°. It therefore became necessary to re-examine the keto-compound.

Tribromophenol bromide was first described by Benedikt (*Annalen*, 1879, 199, 127), who prepared it by adding excess of bromine water to a dilute aqueous solution of phenol. He stated that after repeated crystallisation from chloroform it melted constantly at 118°, and that bromine was evolved only on heating the substance to about 125°. The compound has since been studied by other workers, including Werner (*Bull. Soc. Chim.*, 1885, [iii], 43, 372) and Thiele and Eichwede (*Ber.*, 1900, 33, 673); these authors, however, give no melting point, but Kastle (*Amer. Chem. J.*, 1902, 27, 31) confirms the pre-

viously recorded melting point. The method adopted by Kastle in preparing the substance did not differ essentially from Benedikt's original method, and consisted in adding a dilute solution of phenol to bromine water containing a slight excess of bromine, shaking vigorously, and allowing the precipitate to remain in contact with the liquid for several hours. The precipitate was filtered off, drained on porous earthenware, and left in the air to dry. It was finally crystallised from chloroform.

To prepare tribromophenol bromide, a solution of 2.4 grams of phenol in a considerable volume of water was gradually added to bromine water containing 19 grams of bromine, no particular care being taken to have all the bromine in solution. After each addition of phenol, the bottle was vigorously shaken, and when all the phenol was added the mixture was put aside in a dark cupboard for three days. The precipitate was then pumped off, drained thoroughly on porous earthenware, and dried in a vacuum over sulphuric acid. On dissolving the dry, buff-coloured powder in warm ethyl acetate, a red solution was obtained, from which, on cooling, orange-yellow prisms were deposited. This product melted at 144° but evolved bromine, and was identical in appearance with the product from sulphoanisic acid; a mixture of the two substances intimately ground together melted at 143° , bromine being evolved at the melting point. On recrystallising the product twice from chloroform, the melting point rose to 146° , but bromine vapours were liberated at 143° . Another portion which had been twice recrystallised from ethyl acetate melted at $148-149^{\circ}$, bromine being given off at 145° . In each case the crystals deposited from chloroform were of a paler yellow colour than those from ethyl acetate. It was possible that some change in the substance had been effected by the action of ethyl acetate in the first instance; a second preparation, however, treated in an almost identical way, but crystallised only from chloroform, melted at 143° , giving off bromine at this temperature.

An attempt was now made to lower the melting point by other means. A third preparation was allowed to dry in the air instead of in a vacuum over sulphuric acid. During this process, the crisp powder, although left on a porous plate in the dark, became somewhat tacky, and slightly paler in colour. When a portion of this product was crystallised from chloroform, small yellow plates were obtained which appeared to be homogeneous, but these melted only gradually between 116° and 120° and lost bromine at 123° . On recrystallisation from the same solvent, prisms of considerable size, and yellow in colour but exhibiting red patches, were obtained. This product melted at $133-134^{\circ}$. A further recrystallisation gave the substance in the beautiful prismatic form melting at $141-142^{\circ}$. A

quantity of tribromophenol was obtained from the original mother liquors, and quite a large proportion of this substance, melting at 93—95°, was extracted by light petroleum from a specimen of the crude buff precipitate which had been left exposed to the air for several days.

That the substance is the tribromophenol bromide described by other authors appears from the following facts :

(1) When powdered and gently warmed with a solution of sodium sulphite, it is converted into tribromophenol (m. p. 90—91°).

(2) When gently warmed with strong sulphuric acid, it is converted into the isomeric tetrabromophenol (m. p. 110—111°).

(3) When heated with silver nitrate solution, it is converted into *m*-dibromoquinone (m. p. 130—131°):

0.1620 gave 0.2957 AgBr. Br = 77.67.

$C_6H_2OBr_4$ requires Br = 78.05 per cent.

The highest melting point observed was that of a specimen recrystallised from ethyl acetate, namely, 148—149°. This specimen gave off bromine vapour before melting, at 145°, as also did one or two other specimens melting at a high temperature.

Crystallography.—Tribromophenol bromide crystallises from chloroform in yellow prisms, or in six- or eight-sided plates, belonging to the rhombic system; the crystals sometimes attain a considerable size, one or two having been grown a centimetre long. The faces are very brilliant, but the crystals seem to grow under a strain, as considerable distortion is frequently evident on measurement, and the pinacoid faces generally exhibit a wavy surface. The larger crystals are usually cracked across the long axis. When kept for some time, slight decomposition appears to set in even in the dark, and the crystals develop patches of deep red colour similar to that of bromine.

The following are the details of crystallographic measurement :

System.—Rhombic.

Axial Ratios.— $a : b : c = 0.7945 : 1 : 1.5921$.

Habit.—Prisms, elongated in the direction of the *a* axis, or six- or eight-sided plates, flattened parallel to (001).

Forms present.— $b = \{010\}$. $c = \{001\}$. $o = \{111\}$. $o' = \{212\}$.

Angles observed.	Number of observations.	Limits.	Mean.	Calculated.
$b : o (010) : (111)$	21	$54^{\circ} 8' - 54^{\circ} 40'$	$54^{\circ} 30'$	$54^{\circ} 36'$
$c : o (001) : (111)$	24	$68 25 - 68 56$	$68 39$	—
$c : o' (001) : (212)$	18	$64 53 - 65 30$	$65 9$	$65 6$
$o : o (111) : (1\bar{1}\bar{1})$	17	$42 25 - 42 49$	$42 37$	$42 42$
$o : o (111) : (\bar{1}11)$	20	$93 27 - 94 2$	$93 38$	—
$o : o' (111) : (212)$	15	$15 35 - 16 1$	$15 52$	$15 51$
$o' : o' (212) : (21\bar{2})$	7	$49 35 - 49 51$	$49 44$	$49 48$
$o' : o' (212) : (2\bar{1}2)$	7	$39 8 - 39 20$	$39 14$	$39 8$
$o' : o' (212) : (\bar{2}12)$	18	$114 31 - 115 8$	$114 47$	$114 56$

Optical Properties.—The optic axial plane is parallel to the form $b\{010\}$; the optic axial angle is very large, and the acute bisectrix is parallel to the axis of a . The dispersion of the optic axes is very marked, $\rho < v$. The double refraction is positive.

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