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TRIBROMO-*tert*-BUTYL ALCOHOL, $C_4H_7OBr_3$.[1]

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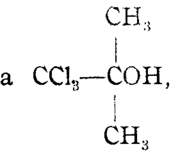
In 1881 C. Willgerodt[2] in studying the action of caustic alkalies on a mixture of chloroform in acetone obtained a crystallin compound which resembled camphor somewhat in odor and taste and consequently excited considerable interest.

By analysis and vapor density determinations it was shown that it is an addition product of acetone and chloroform, having the formula $C_4H_7OCl_3$ or $CHCl_3.(CH_3)_2CO$. It was given the name acetone chloroform and later[3] the structural formula  $CCl_3—\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}OH$, showing it to be trichloro-*tert*-butyl alcohol or the trichloride of acetonic acid. The melting point of trichloro-*tert*-butyl alcohol which has received the commercial name "chloretone," varies according to the amount of water associated with it. The product recrystallized from solvents containing water and allowed to dry in the open air has a melting point near 80°. The anhydrous compound which Cameron and Holly[4] claim has probably never been obtained should, according to them, melt near but above 97°. Willgerodt[5] states that the acetone chloroform described by him, when recrystallized from dilute alcohol and ether, melted at 80–81° and contained exactly 0.5 molecule of water; whereas the product crystallized from carbon disulfide or repeatedly sublimed is anhydrous and melts at 96°.

The following are some of the properties of chloretone. Boiling point 167° (uncorrected), very volatil in the air, readily volatilized with steam. It has a camphorous odor and taste. It is sparingly soluble in water (0.5 per cent.); extremely soluble in ether, alcohol, glacial acetic acid, acetone and chloroform. Soluble also in white neutral oil, and vegetable oils and fats. It is widely used as a therapeutic agent.[6]

I have mentioned these facts relative to chloretone, its manner of formation, etc., in order to compare it with the analogous compound, tribromo-*tert*-butyl alcohol, or "brometone."

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[1] "Brometone" is the commercial name.

[2] *Ber.*, 14, 2451 (1881).

[3] *Ibid.*, 15, 2305 (1882).

[4] *J. Phys. Chem.*, 2, 322 (1898).

[5] *Ber.*, 16, 1585 (1883).

[6] Houghton and Aldrich, *J. Am. Med. Assoc.*, Sept. 23, 1899, p. 77; also *Am. J. Physiol.* (Proceedings), 3, 26 (1900).

This compound is prepared in a similar manner to chloretone, that is, by the action of solid caustic alkalies on a mixture of acetone and bromoform; but it is more difficult to isolate in a pure form. In making chloretone any excess of chloroform can be readily blown off or distilled off. This can be done, but not so readily, with an excess of bromoform and not without considerable loss of the product desired. It can be obtained, however, as a beautiful white crystallin compound, by removing the excess of bromoform, distilling with steam and recrystallizing from a suitable solvent.

It melts at 167–176°, volatilizes in the air but much more slowly than the corresponding compound. At attempt to distil it at ordinary pressure caused decomposition and the evolution of a very irritating gas. No attempt was made to distil it under reduced pressure. It has a camphorous odor and taste. Its solubilities are very similar to those of chloretone. There is no doubt that we have here tribromo-*tert*-butyl alcohol, or the tribromide of acetonic acid, shown by the following analyses which were carried out with a product crystallized from dilute alcohol a number of times and dried in a desiccator over calcium chloride.

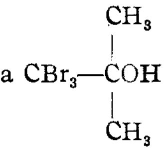
	Calculated for $C_4H_7CBr_3$.	Found.				
		1.	2.	3.	4.	Average.
C.	15.43	15.31	15.24	16.13	15.26	15.48
H.	2.25	2.37	2.26	2.33	2.41	2.34
O.	5.15	...	...	...	...	...
Br.	77.17	76.24	75.44	76.84	76.24	76.19

The following analyses were also made from another product dried over calcium chloride, the last two after long drying:

	Calculated for $C_4H_7OBr_3$	Found.						
		1.	2.	3.	4.	Average.	6.	7.
C.	15.43	15.21	14.58	...	..	14.90	15.7	15.37
H.	2.25	2.19	2.18	...	..	2.19	2.32	2.31
Br.	77.17	76.92	76.26	76.58	77.1	76.72	77.06	77.14

The above analyses and the difficulty of obtaining very closely concordant results would indicate that there is a varying amount of water present in brometone, this being indicated by the carbon and bromine content, which are low, and the hydrogen content, which in general is high.

The analyses are however, sufficiently near to assign to it the formula $C_4H_7OBr_3$ and it has no doubt the structural formula



$$CBr_3—\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}OH$$

similar to that assigned to chloretone by Willgerodt.

Several attempts have been made to obtain acetonic acid from this product as Willgerodt did from chloretone, but although a small amount of a supposedly organic acid was obtained and an attempt made to convert it into the barium salt, the amount was so small that the results obtained were not sufficiently close to demonstrate its formation, although it was probable. What has been said relative to chloretone (Cameron and Holly) is no doubt true of brometone, *viz.*, that the substance contains water, and in varying amounts, that the water cannot be detected or eliminated by mechanical means, that it is not present to form a hydrate. Therefore it is present to form a solid solution. Brometone is used as a therapeutic agent. For its pharmacological action see Houghton and Aldrich.[1]

THE REDUCTION OF THE ANHYDROXIME OF *o*-BENZOYLBENZOIC ACID.

By Robert Evstafieff Rose.

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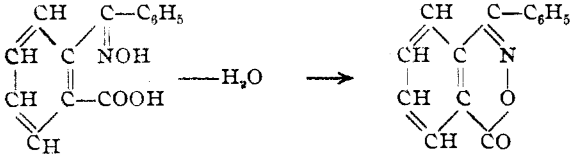
In common with other oximes of aromatic aldehydes and ketones containing a carboxyl group in the *o*-position to the carbonyl that of *o*-benzoylbenzoic acid is incapable of existing in the free state. It loses the elements of water spontaneously when liberated from its alkali salt, yielding what may be termed an anhydroxime thus:



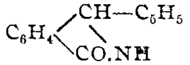
Several representatives of this class of compounds are known, but their chemical behavior has been little studied, though a closely related substance, the oxime of phenolphthalein, has been the subject of thorough investigation. It therefore seemed of interest to examin the behavior of the anhydroxime of *o*-benzoylbenzoic acid more especially towards reducing agents, the analogous compound obtained from phenolphthalein having proved to be readily reducible.

Experiment showed the anhydroxime to undergo quantitative reduction when treated with nascent hydrogen, a stable crystallin reduction product being formed.

For this substance the following formulas must be considered:

I. 

$$C_6H_4\left\langle\begin{matrix}CH_2-C_6H_5\\CONH_2\end{matrix}\right.$$

II. 

of which the first shows the reduction product as the amide of *o*-benzyl-

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[1] *Am. J. Physiol.* (proceedings), 8, 18 (1903).