

XLIV.—CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF EDINBURGH.

No. I. *On Tertiary Butyl Mercaptan.*

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THE known readiness with which zinc oxide acts on tertiary butyl iodide, as described in a previous paper communicated to this Society (Trans., 1880, 239), led the author, when in search of a method for the preparation of tertiary butyl sulphide, to try the action of zinc sulphide on the same iodide. It should be mentioned that the experience with zinc oxide, which yielded as chief products zinc iodide, water, and triisobutylene, did not seem to give much promise of reaching the desired result with the sulphide. On heating a mixture of the substances, however, on a small scale, unmistakable evidence of the formation of an organic sulphur compound was afforded by the extremely unpleasant and characteristic odour produced.

Various experiments were then made on a larger scale, but considerable difficulties were met with before the conditions for obtaining the best results were ascertained. It was found, for instance, that the extent to which the iodide underwent decomposition depended very greatly upon the sample of zinc sulphide employed; although the different experiments were made under conditions which were otherwise similar. With one commercial sample, the removal of iodine from the iodide became complete very rapidly, whilst with others it was found impossible to accomplish complete decomposition.

The first method employed for carrying out the reaction was as follows:—50 grams of tertiary butyl iodide were mixed with

200 grams of nearly anhydrous alcohol; 20 grams of (almost white) commercial zinc sulphide were added, and after standing for a few hours in the cold, the mixture was heated in a flask with a reflux condenser for about six hours. The alcohol was then distilled off as completely as possible by means of a water-bath, and the distillate diluted with about twice its own volume of water. A small portion separated out as a layer on the top of the aqueous alcohol. This was separated, dried over calcium chloride, and fractionated. It began to boil at about 65°, and the boiling point gradually rose to 100°, below which temperature more than half distilled over. At 107°, the distillation practically ceased, and almost nothing came over till 170° was reached. Then between 180° and 190°, nearly all the remainder distilled; at about 190°, decomposition, with darkening, began.

On repeatedly fractionating the fraction boiling at the lowest temperature, a large proportion of it was found to boil between 65° and 70°. This portion was quite free from iodine, and was sealed up for analysis. Its low boiling point seemed to indicate that it could not be tertiary butyl sulphide.

The normal sulphide boils at 182° (Grabowsky and Saytzeff, *Annalen*, **171**, 254); isobutyl sulphide boils at 170.5° (Beckmann, *J. pr. Chem.* [2], **17**, 446); secondary butyl sulphide boils at 165° (Reymann, *Berichte*, **7**, 1288).

Analyses gave numbers which correspond with the composition of tertiary butyl mercaptan:—

- I. 0.2262 gram substance gave 0.4405 gram CO₂ and 0.2187 gram H₂O.
 II. 0.2306 gram substance gave 0.4481 gram CO₂ and 0.2215 gram H₂O.

	Calculated for (CH ₃)CSH.	Found.	
		I.	II.
C	53.33	53.11	52.99
H	11.11	10.74	10.67
S	35.55	—	—

In several subsequent experiments, made in exactly the same way, with other commercial samples of zinc sulphide, and also with a special laboratory preparation, the product was not in any case obtained free from iodine.

By a simplification of the foregoing method complete removal of the iodine and uniform results were obtained.

Preparation of Tertiary Butyl Mercaptan.

The zinc sulphide to be employed was precipitated from the aqueous solution of zinc sulphate by passing in sulphuretted hydrogen,

ammonia being added from time to time to prevent the liquid from becoming so strongly acid as to prevent further action of the sulphuretted hydrogen. Owing to the great difficulty of efficiently washing the bulky precipitate of freshly-prepared zinc sulphide, the precipitate was at first only partially washed. Then it was dried at the ordinary temperature (whereby its bulk became very greatly decreased), finely powdered, thoroughly washed with water to remove ammonium sulphate, and again dried at the ordinary temperature. 20 grams of this zinc sulphide were heated in a retort on a water-bath with 50 grams of tertiary butyl iodide, till (at about 45°) a manifest action set in. To prevent loss of the very volatile product of the action, the retort was connected with a U-tube placed in a freezing mixture. The digestion was afterwards carried on at a gentle heat for about two hours, until rapid evolution of sulphuretted hydrogen was observed. This gas was not given off at the beginning of the operation. The contents of the retort were then distilled off as completely as possible from a water-bath. The distillate, which was collected in a freezing mixture, was dried over calcium chloride and then fractionated. It was quite free from iodine. A large proportion of it was found to be of low boiling point, and a large fraction boiling between 65° and 67° was employed for analysis:—

0.1878 gram substance gave 0.3619 gram CO_2 and 0.1861 gram H_2O .

These numbers correspond to 52.55 per cent. carbon, and 11.01 per cent. hydrogen, whilst tertiary butyl mercaptan requires 53.33 per cent. carbon, and 11.11 per cent. hydrogen.

This product was believed to be more nearly free from the product of high boiling point than that first analysed, although the percentage of carbon found was somewhat lower. The product of high boiling point is much richer in carbon than the mercaptan, so that the presence of a small quantity of it in the mercaptan would greatly raise the apparent carbon percentage of the latter. On the other hand, the extreme volatility of the mercaptan gave rise to slight loss at the commencement of each combustion, a fact which the smell of the mercaptan rendered unquestionable.

Properties of Tertiary Butyl Mercaptan.

Tertiary butyl mercaptan, obtained as described above, is a very volatile liquid, boiling at $65\text{--}67^{\circ}$. It solidifies to a white, semi-transparent mass when placed in a freezing mixture of snow and salt. It possesses an overpowering and characteristic disagreeable odour, which, however, is not so offensive as that of some of the lower homo-

logues. It forms voluminous, white, insoluble compounds when mixed with aqueous solutions of mercuric chloride and of silver nitrate. The compound formed with the latter becomes black on standing for some hours, and quickly on boiling, owing to the formation of silver sulphide.

The fraction of high boiling point (over 180°), previously mentioned, was fractionated, and a small quantity of that boiling between 177° and 185° was used for combustion. Determinations of the carbon and hydrogen were made in order to find out the nature of the difference between the products of low and of high boiling points respectively, but the quantity available was too small to investigate the matter fully.

It was obvious from the formation of the mercaptan that some of the C_4H_9 groups of the original iodide must have lost hydrogen, and this fact, viewed in connection with the formation of tri-isobutylene, when zinc oxide acts on tertiary butyl iodide (Trans., 1880, 241), rendered it highly probable that polymeric isobutylene derivatives might be formed here also. The evolution of sulphuretted hydrogen could also only occur by similar loss of hydrogen from C_4H_9 -groups. The only other product likely to be formed is tertiary butyl sulphide, the boiling point of which would probably lie not much below 160° . The boiling point of tri-isobutylene is $177.5-178.5^{\circ}$ (Lermontoff), so that a separation of these two substances, if mixed, would be extremely difficult with the small quantity which was available. The figures obtained on combustion gave a result which would represent a mixture of tertiary butyl sulphide and tri-isobutylene:—

0.182 gram substance gave 0.5227 gram CO_2 and 0.2161 gram H_2O .

	Calculated for.		
	$(C_4H_9)_2S$.	C_nH_{2n} .	Found.
C.....	65.75	85.71	78.31
H.....	12.32	14.28	13.19

This part of the subject is at present under investigation.

It is of interest in connection with the foregoing and with the known difference of behaviour towards reagents of the isobutyl and tertiary butyl iodides, to note that Grabowsky and Saytzeff (*Annalen*, 171, 255), prepared isobutyl sulphide by acting on isobutyl iodide with an alcoholic solution of potassium sulphide; but in trying to carry out an analogous reaction with the tertiary iodide, they failed to obtain anything more than "traces of a liquid possessing the characteristic garlic odour, whilst the greater portion of the iodide decomposed into hydriodic acid and butylene." In view of the

fact that alcoholic solution of potassium sulphide does not react in the usual way with the tertiary iodide, Saytzeff states (*ibid.*, **171**, 258) that a student (Ivanoff) was (in 1874) about to try the action upon the latter of the sulphides of other metals, in imitation of Butlerow's method for obtaining tertiary butyl cyanide, but apparently no results of any such experiments have been published.

Beckmann (*J. pr. Chem.*, [2], **17**, 446) mentions that by distilling isobutyl potassium sulphate with aqueous solution of potassium sulphide, besides isobutyl sulphide (B. P. 170.5°), he obtained another sulphur compound boiling at 88°, the nature of which he did not then know. The substance was most likely isobutyl mercaptan, which had been previously described by Humann (*Annalen*, **95**, 256) as a liquid boiling at 88°.
