XCII.—*The Isomeric Dibromethylenes.*

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THE experiments described in this paper were undertaken with the object of preparing the two dibromethylenes of the formulæ, $\begin{array}{c} \text{H} \cdot \text{C} \cdot \text{Br} \\ | \\ \text{H} \cdot \text{C} \cdot \text{Br} \end{array}$ and $\begin{array}{c} \text{H} \cdot \text{C} \cdot \text{Br} \\ | \\ \text{Br} \cdot \text{C} \cdot \text{H} \end{array}$, in view of the fact that such an example of the isomerism of two unsaturated carbon compounds, composed solely of univalent atoms linked to carbon, would be of theoretical interest. In addition to the isomerides above mentioned, a third dibromethylene, of the formula $\text{CH}_2\text{:CBr}_2$, is theoretically possible, but only two substances having the empirical formula $\text{C}_2\text{H}_2\text{Br}_2$ have so far been prepared. One of these boils at 110° , and is represented by the formula $\text{CHBr}:\text{CHBr}$, whilst to the other, which boils at 91° , the unsymmetrical structure $\text{CH}_2\text{:CBr}_2$ is usually ascribed; although the behaviour of the substance towards oxygen, with which it unites to form bromacetyl bromide, $\text{CH}_2\text{Br}\cdot\text{COBr}$, is more easily explained on the assumption that the formula $\text{CH}_2\text{Br}\cdot\text{CBr}$, advanced by Fittig, represents its structure. (See also Michael, *Amer. Chem. J.*, 1883, 5, 192). An examination of the literature in connection with the dibromethylenes seems to point to the existence of the third isomeride, a liquid possessing a higher boiling point than the two previously mentioned. Thus Tawildaroff (*Annalen*, 1875, 176, 22), by the action of vinylic tribromide on sodium ethoxide solution, obtained a liquid which he separated by repeated fractionation into dibromethylene boiling at 91° , and a liquid of the same composition boiling at 157° . Again, Sabancéff (*Annalen*, 1875, 178, 115), in the preparation of dibromethylene by the union of acetylene with bromine, obtained an oil which, on distillation, left a residue boiling above 115° ; this, after purification by steam distillation, was analysed and found to have the composition represented by the formula $\text{C}_2\text{H}_2\text{Br}_2$. This method was relinquished in favour of the

preparation from acetylene tetrabromide by reduction with zinc, which Sabanéeff subsequently adopted, as he found it difficult to purify the product of the former reaction and to obtain a satisfactory yield; but a repetition of this as well, as of Tawildaroff's experiment, seemed of interest.

Action of Sodium Ethoxide on Vinylic Tribromide.

The possibility of the formation of two dibromethylenes in this reaction is evident from a glance at the formula of vinylic tribromide. If we consider the arrangement in which each hydrogen atom is vertically above or below a bromine atom to be the more probable, we can conceive hydrogen bromide to be removed in two ways, with formation respectively of the *trans*-modification of symmetrical, and of unsymmetrical dibromethylene, as shown in the following equation:

If we accept the formula given in the second equation, the only difference is that we should get the *cis*- instead of the *trans*-modification, if the former is sufficiently stable to be capable of existing under the conditions of the reaction. A glance at the following equation will render this evident:

These speculations are in accord with the results obtained by Tawildaroff, but Michael (*Amer. Chem. J.*, 1883, 5, 192), on repeating this experiment, obtained only unsymmetrical dibromethylene, and attributed Tawildaroff's observation to impurity in the vinylic tribromide which the latter prepared by the action of bromine on ethylenic dibromide. It seemed to me, however, possible that an alteration of the concentration of the sodium ethoxide might give rise to symmetrical dibromethylene, as a similar observation has been made with regard to the addition of HBr to vinylic bromide; this substance is converted into ethylenic dibromide by the action of a solution of HBr saturated at 6°, but ethylidenic bromide is formed if the solution of the acid be previously diluted with half its volume of water (Reboul, *Annalen*,

1870, 155, 29 and 212). To settle this point, the following experiments were carried out :

Experiment I.—A solution of vinylic tribromide (78·5 grams) in its own volume of absolute alcohol was cooled in a freezing mixture, and a solution of sodium ethoxide, containing the theoretical quantity of sodium dissolved in 10 times its weight of absolute alcohol, was added through a tap funnel. The solution was then heated on a water bath to expel bromacetylene, as recommended by Tawildaroff, but in this case no evolution of gas was noticed, although the odour of the substance was distinctly perceptible. The product was then poured into water, and the oil which separated was subjected to distillation. The result was similar to that obtained by Michael ; practically the whole passed over below 110° , leaving a small, dark-coloured residue. From this residue, by steam distillation, a few drops of a colourless oil were obtained ; on distilling this, the temperature rose rapidly to 180 — 190° , when a small quantity of unchanged vinylic tribromide passed over. The fraction below 110° , on re-distillation, gave two fractions, 88 — 92° and 92 — 110° ; the first of these was fairly pure α -dibromethylene, and the second also evidently consisted largely of the same substance, as a solid quickly separated from it on exposure to the air. When the higher fraction was subjected to refractionation, the boiling point rose steadily until, after two or three distillations, a fraction was collected, boiling between 150° and 160° . This fumed strongly on exposure to air, and dissolved easily and completely in dilute soda solution. In view of Demole's observation of the behaviour of α -dibromethylene on heating in air, the identification of this liquid as bromacetyl bromide, b. p. 149° , was easy. This observation was made subsequently to Tawildaroff's work ; and as the latter doubtless conducted the fractionation in air, it seems probable that the substance he obtained was bromacetyl bromide, possibly contaminated by vinylic tribromide, or impurities accompanying the latter, from which it would be difficult to separate the bromacetyl bromide by distillation. In order to prevent this oxidation in the later experiments, all the operations, subsequent to the addition of the sodium ethoxide, were conducted as far as possible in an atmosphere of carbonic anhydride ; thus the oil was dried over calcium chloride in an atmosphere of this gas, and afterwards filtered into a distillation apparatus filled with carbonic anhydride, a stream of the gas being directed into the funnel during the filtration. In this way, loss of substance due to polymerisation was also avoided.

Experiment II.—The calculated quantity of sodium ethoxide solution was added to vinylic tribromide (78 grams) cooled in a freezing mixture, and the product treated as described above. The result of the fractionation may be briefly stated as follows :

	Fract. I, 89 — 90° .	II, 90 — 94° .	Residue.
Weight in grams.....	40·9	1·5	1 (approx.)

The rapid separation of solid from fraction II on exposure to air showed it to be substantially identical with I. The dark-coloured residue probably contained unchanged vinylic tribromide. In this experiment the yield of liquid boiling at 89—90° was 75 per cent. of the theoretical.

In the two previous experiments, the sodium ethoxide solution was added to the vinylic tribromide in order to avoid loss of substance through formation of bromacetylene; but as Tawildaroff allowed the tribromide to run into the sodium ethoxide solution, this method was next tried, in order to determine whether it had any influence on the course of the reaction.

Experiment III.—A slight excess of sodium ethoxide solution was here taken to replace that which was used up in the further reduction of the dibromethylene to bromacetylene. This was cooled in a freezing mixture, and the vinylic tribromide (100 grams) was quickly added through a tap funnel, after the air in the apparatus had been displaced by nitrogen. The conditions were otherwise the same as in experiment II. The formation of bromacetylene was here noticed, both on account of its peculiar odour and the production of white fumes on contact with the air.

Result of fractionation :

	Fract. I, 88—89°.	II, 89—91°.	III, 91—95°.	Residue.
Weight in grams.....	1·3	40·4	4·3	0·8

From I, solid rapidly separated on exposure to air. Fraction III, which passed over mostly at 91°, was redistilled; of the 3·8 grams which were transferred, 2·1 grams distilled over at 91—92°, whilst the small quantity which came over above this temperature deposited a solid on exposure to air; *a*-dibromethylene was, therefore, the sole product of the reaction, the only effect of reversing the order of addition being to diminish the yield, as was to be expected.

Experiment IV.—In this case, a more dilute solution of sodium ethoxide was used; 78 grams of vinylic tribromide dissolved in four times its weight of alcohol was cooled in a freezing mixture, and the calculated quantity of sodium ethoxide solution (1 sodium in 10 of alcohol) added. The yield was smaller than in the previous experiments, but the result was similar.

	Fract. I, 89—90°.	II, 90—95°.	Residue.
Weight in grams.....	24·3	3·4	0·8

Fraction II, on redistillation, gave 2·4 grams, boiling at 89—91°.

These experiments seem to prove that unsymmetrical dibromethylene is the only product of the primary action of sodium ethoxide on vinylic tribromide.

Preparation of Symmetrical Dibromethylene by the Union of Acetylene with Bromine.

The conditions for the direct formation of this substance from acetylene and bromine were first established by Sabanéeff (*loc. cit.*), who proved that it was necessary to use a sufficiently dilute solution of bromine, and to have the acetylene present in excess; the calculated quantity of bromine was added to alcohol saturated with acetylene, the saturation with acetylene and addition of bromine were several times repeated, and the product was finally poured into water. The oil which separated was fractionated, the fractions, 50—80° and 106—115°, were assumed to be products of the action of bromine on alcohol, and accordingly set aside, the residue, after purification, having the formula $C_2H_2Br_2$.

If it be assumed that the product of this reaction was the dibromethylene boiling at 110°, then the fraction containing the bulk of the dibromethylene must have been rejected. It seemed to me probable, however, that the substance Sabanéeff obtained was isomeric with the one subsequently prepared, as the latter, as will be shown later, probably has the *trans*-configuration, whilst the product of the direct union of acetylene and bromine, if stable, should be the *cis*-modification, as indicated in the following equation.

In order to avoid bye-products, which might render purification difficult, the reaction was carried out in aqueous solution. Acetylene, prepared by the action of water on calcium carbide, was passed into a series of flasks, each containing about a litre of water; when the water in the first two flasks was saturated, these were removed, and after having been refilled were attached to the end of the apparatus; in this way, loss of acetylene was avoided. To the aqueous solution of the gas, considerably less than the calculated quantity of a saturated solution of bromine was added, and the mixture was then allowed to remain in a dark cupboard for a few days until it became colourless. As no separation of oil took place, and extraction with ether could not be economically carried out with such large quantities of liquid, the solution was heated to boiling, and the oil which passed over was collected. The yield was exceedingly small, but as the object was merely to establish the identity of the product, the process was carried on for about a month, when a sufficient quantity was obtained

for further examination. The united distillates were extracted with ether, and the ethereal solution, after drying, was subjected to distillation. About 10 grams of an oil boiling at 108—110° were obtained, the united residues of the fractionation weighing about 4 grams. When these residues were again distilled, about half passed over between 110 and 115°, and the temperature then rose rapidly to over 200°; this was doubtless due to the presence of a small quantity of acetylene tetrabromide.

The product of the union of acetylene with bromine is thus evidently identical with the dibromethylene obtained by the reduction of acetylene tetrabromide, but we are not entitled to conclude from this result that dibromethylene has the *cis*-configuration, as we might expect a substance of this formula to be unstable, and to tend readily to pass into the *trans*-modification. If we glance at the equation representing the formation of dibromethylene from acetylene tetrabromide, we see that either isomeride may be formed depending on the arrangement of the atoms which we assume to represent the structure of the tetrabromide, thus :

Sabanéeff has shown (*Annalen*, 1883, 216, 252) that the only product of the reduction of acetylene tetrabromide by means of zinc, under the conditions there stated, is the dibromethylene boiling at 110°; when commercial bromine was used, some $\text{C}_2\text{H}_2\text{Cl}_2$ and $\text{C}_2\text{H}_2\text{ClBr}$ were formed, owing to impurity present in the bromine. On repeating Sabanéeff's experiment, the product, after fractionation, gave 203 grams of liquid, boiling at 109—111°, whilst the united residues above 120° only weighed about 19 grams. These residues, on distillation under reduced pressure, were proved to consist to the extent of approximately one-third of their weight of acetylene tetrabromide. It is therefore evident that only one dibromethylene is formed in this reaction, and as the arrangement of atoms represented in the second equation appears to be the more probable, we conclude that the product has the *trans*-configuration. In order to test this view, an attempt was made to prepare dibromethylene by the addition of hydrogen bromide to bromoacetylene, from which the *trans*-modification should result, as is shown by the following equation.

The bromacetylene, prepared from dibromethylene by the action of an alcoholic solution of caustic soda, using the proportions recommended by Sabanéeff (*Ber.*, 1885, 18, 374), was condensed in a freezing mixture, 50 grams of $C_2H_2Br_2$ yielding 13 grams of C_2HBr . A saturated solution of hydrogen bromide, slightly in excess of that required by theory, was added to the liquid while a current of nitrogen was being passed through the apparatus. The U-tube containing the two substances was then allowed to stand for two days, after which the unchanged C_2HBr was expelled by heating on a water bath in a current of carbonic anhydride, and the brown, somewhat viscous oil, after treatment with soda solution, washing, and drying, was subjected to distillation in an atmosphere of carbonic anhydride. The temperature rose steadily to about 110° , and then showed signs of remaining stationary, but the amount of oil which passed over was much too small to admit of purification. The residue, which represented the bulk of the original liquid, decomposed on further heating; hydrogen bromide was given off, and a charred mass remained. Another experiment was accordingly made, using 100 grams of $C_2H_2Br_2$, and the product was distilled under diminished pressure. The lower fractions, on re-distillation at atmospheric pressure, yielded a small quantity of a colourless oil boiling at $110-113^\circ$; this had the odour of symmetrical dibromethylene, and seemed sufficiently pure for analysis, although the boiling point was slightly high.

Found: Br = 86.3. Calculated for $C_2H_2Br_2$: Br = 86.02 per cent.

The spontaneous inflammability of bromacetylene on exposure to air rendered operating on a large scale difficult, but the properties of the small quantity of liquid obtained in this experiment, and the data ascertained, left no doubt as to the identity of the substance.

The higher fractions were distilled under diminished pressure, and a small quantity of a yellow liquid, which passed over between 120° and 130° (pressure approx. 30 mm.), was collected. This did not solidify when placed in a freezing mixture, but when stirred up with a quantity of alcohol insufficient for complete solution, part of the oil was slowly dissolved, and the residue became viscous and finally solid. The solid, on recrystallisation from alcohol, was obtained in long, needle shaped crystals, which melted at $120-121^\circ$. The melting point of the substance, its crystalline form, and sparing solubility in alcohol, pointed to its identity with symmetrical tribromobenzene (m. p. 120°), but the quantity obtained was not sufficient to enable me to establish this by analysis. The formation of this substance by the polymerisation of bromacetylene is well known, and its presence as a product of this reaction is thus explained.

The results of this communication may be summarised as follows:

Only one substance of the formula $C_2H_2Br_2$, namely, unsymmetrical dibromethylene, is obtained by the action of sodium ethoxide on vinylic tribromide.

The same modification of symmetrical or β -dibromethylene is obtained by each of the three following methods: 1. Union of C_2H_2 with Br_2 . 2. Union of C_2HBr with HBr . 3. Reduction of $C_2H_2Br_4$.

The formation of this substance by method 2, and the probable instability of the *cis*-modification, point to the formula

$$\begin{array}{c} H \cdot C \cdot Br \\ | \\ Br \cdot C \cdot H \end{array}$$

for the β -dibromethylene at present known