XLV.—*Researches on Di-methyl.*

By WM. H. DARLING.

Being the results of an investigation for which the Dalton Chemical Scholarship at Owens College was awarded, October, 1867.

THE synthesis of carbon compounds forms perhaps the most important and interesting branch of modern chemical inquiry.

By the most recent developments of these synthetical processes it has been ascertained, that the chemical properties of a carbon compound depend upon the position of the atoms of which its molecule is built up.

From Frankland's original observations concerning the difference between the action of chlorine on the so-called dimethyl $\left. \begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix} \right\}$ obtained by the electrolysis of an alkaline acetate, and on the hydride of ethyl $\left. \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{H} \end{smallmatrix} \right\}$, obtained from ethyl compounds, the existence of a difference in the four combining powers of a carbon atom was rendered probable.

The subsequent researches of Schorlemmer have, however, proved that only one hydrocarbon of the formula C_2H_6 exists, inasmuch as he succeeded in preparing ethyl chloride from the hydrocarbon di-methyl $\left. \begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix} \right\}$, obtained by the electrolytic decomposition of an alkaline acetate (Proc. R. Soc., xiii., 225); as well as from ethyl-hydride, obtained from ethyl compounds.*

It appeared of great interest to repeat this synthesis, and to prepare the chloride in larger quantity, from which to obtain ethyl compounds and ascertain their chemical and physical properties.

At the request of Mr. Schorlemmer, I undertook this investigation. I take this opportunity to express my thanks to that gentleman, and also to Professor Roscoe, for the kind assistance rendered to me throughout this research.

* Chem. Soc. J. [2], ii, 262.

I. PREPARATION OF DI-METHYL BY SCHÜTZENBERGER'S PROCESS.

When peroxide of barium acts on acetic anhydride, a gas, stated to be di-methyl, is given off, the reaction being represented as follows:—

It was found that if the peroxide was heated with the anhydride, as Schützenberger directs, a violent explosion occurred, breaking the apparatus. In order to avoid this, the peroxide was mixed with dry sand; this had the desired effect, if the decomposition was allowed to begin at once. If, however, the flask containing the mixture was cooled to begin with, the action after a time became so violent, probably owing to the formation of peroxide of acetyl, that explosions occurred. 20 grms. of anhydride were weighed into a two-ounce flask, and an intimate mixture, consisting of 20 grms. of powdered peroxide of barium and 40 grms. of dry sand, was poured in, mixed by shaking and immediately connected with a bent glass tube, whereby all the air was displaced. The gas evolved was collected in a Pepys gas-holder, and afterwards displaced by pressure; it was purified by passing first through a strong solution of caustic potash to absorb the carbonic acid, afterwards through concentrated sulphuric acid to absorb any vapour of acetic anhydride present. The gas thus prepared burnt with a feebly luminous flame. In order to form the chloride, the gas thus prepared was treated with an equal volume of chlorine in the following manner:—A white glass bottle of about 2.5 litres capacity, full of water, was exactly half filled with the purified gas in a pneumatic trough, the remaining water displaced by pure chlorine, and the bottle tightly corked. The bottle thus filled was exposed, until nearly colourless, to diffused sunlight, after allowing time for the two gases to mix, and the action was completed by means of direct sunlight. The bottle was then opened under warm water; the hydrochloric acid absorbed was equal to half the capacity of the bottle. The remainder

* Comptes Rendus, 1865, lxi, 487.

of the gaseous contents not absorbed was displaced by warm water into a receiver, in which a few pieces of stick potash were placed, and which was surrounded by a freezing mixture of salt and ice. In this tube a small quantity of liquid was condensed. After using the anhydride obtained from one pound of phosphorus, with the exception of a small quantity reserved for future analysis of the gas, the total volume of liquid obtained did not exceed 25 c.c., and began to boil at 40° C., the temperature rising up to 80° C. This quantity proved too small to admit of being fractionated, in order to separate any more highly chlorinated products.

In order to ascertain the cause of so small a yield of chloride, the gas was analysed, according to Bunsen's method, after freeing it from carbonic acid and vapour of anhydride by means of caustic potash. It was first tested for carbonic oxide, by means of cuprous chloride, and yielded the following result:—

A.

	Volume.	Pressure.	Temp. C.	Vol. at 0° C. and 1m. Pressure.
Gas originally employed (moist) ..	122·7	0·7151	14·0	83·47
After absorption of carbonic oxide (dry)	116·65	0·7273	17·0	79·86

The composition, as determined by analysis A, is

Carbonic oxide	3·61
C_nH_{2n}	}
C_2H_6	
$C H_4$	
	79·86
	<hr/> 83·47

The following absorption analysis B, was made with fuming sulphuric acid to determine the presence of olefines.

B.

	Volume.	Pressure.	Temp. C.	Vol. at 0° C. and 1m. Pressure.
Original volume of gas (dry)	116·65	0·7273	17·0	79·86
After absorption with fuming sul- phuric acid (dry)	119·40	0·7082	18·0	79·32

Hence the composition from B is

Carbonic oxide	3.61
C_nH_{2n}	0.54
C_2H_6 }	79.32
C_2H_4 }	
	<hr/> 83.47

For the determination of the remaining constituents, which could only consist of di-methyl and methyl hydride, a combustion analysis was made.

C.

	Volume.	Pressure.	Temp. C.	Vol. at 0° C. and 1m. Pressure.
Original volume (moist)	203.5	0.1684	18.0	32.16
After addition of air (moist).....	527.1	0.4783	19.4	235.4
" oxygen (moist) ..	618.5	0.5647	21.5	323.8
" explosion (moist)	551.5	0.4992	20.2	256.4
" absorption of carbonic acid (dry).....	495.2	0.4658	16.2	217.8

Original volume of gas 32.16 = A

Contraction 67.40 = C

Carbonic acid 38.60 = B.

Since 1 volume of di-methyl gives 2.5 volumes of contraction and 2 volumes of carbonic acid, and 1 volume of methyl hydride gives 2 volumes of contraction and 1 volume of carbonic acid, then, if y represents the former gas and x the latter,

$$\begin{aligned} x + y &= A \\ x + 2y &= B \\ y &= B - A & x &= 2A - B. \end{aligned}$$

By substituting the numerical values,

$$\begin{aligned} x + y &= 32.16 & x + 2y &= 38.6 \\ y &= 38.6 - 32.16 & x &= 64.32 - 38.6 \\ y &= 6.44 & x &= 25.72. \end{aligned}$$

The contraction C gives a third formula,

$$2x + \frac{5}{2}y = C$$

$$x + y = A$$

$$y = 2(C - 2A)$$

$$x = A - 2(C - 2A).$$

Again substituting values,

$$2x + \frac{5}{2}y = 67.4$$

$$x + y = 32.16$$

$$y = 2(67.4 - 64.32)$$

$$x = 32.16 - 2(67.4 - 64.32)$$

$$y = 6.16$$

$$x = 26.00.$$

Taking the mean of the results,

$$x = 25.86$$

$$y = 6.30.$$

From these analyses the following numbers were obtained :—

Carbonic oxide	3.58	4.29
Olefines	0.54	0.63
C ₂ H ₆	15.49	18.57
C H ₄	63.84	76.51
	<hr/>	<hr/>
	93.45	100.00

This analysis clearly shows that Schützenberger's description of the above decomposition is incorrect, the greater part of the gas consisting of hydride of methyl.

This method being found not to yield the required product, and not to be pure di-methyl, I endeavoured to procure this substance in quantity by the action of zinc upon methyl iodide.

II. PREPARATION OF DI-METHYL BY FRANKLAND'S PROCESS.

In order to prepare pure di-methyl, I took advantage of the directions given by Schöyen* for the preparation of pure di-ethyl.

Into stout glass tubes closed at one end, metallic zinc made rough on its surface was introduced; the open end was then softened before the blow-pipe, thickened, and drawn out into a strong capillary, which was bent twice at right angles, as described by Frankland. Through this capillary the methyl iodide was introduced, and afterwards the ether, equal in volume to that of the iodide, both of which had been dried as far as

* Ann. Ch. Pharm, cxxx, 233.

possible over metallic sodium. The air in the tube was displaced by boiling the ether and closing the capillary, and the end was thickened after cooling the tube.

Tubes thus prepared were maintained at a temperature of 130°C ., until all the zinc was dissolved, then allowed to cool, and afterwards opened by softening the end of the capillary before the blow-pipe, when any marsh-gas, which by presence of some moisture might have formed, escaped.

The tube, after heating until the contents began to boil, was again sealed, and heated at 150°C . for several hours.

After the tubes had attained the temperature of the room, they were immersed in a mixture of salt and ice; one end of a narrow tube of thick caoutchouc was drawn over the capillary, the other end being attached to a gas holder containing a saturated solution of common salt; and the end of the capillary was broken off. The gas then rushed into the holder, the internal pressure frequently projecting some of the liquid contents into the holder, where, in contact with the water, decomposition took place, it being almost impossible to decompose all the zinc-methyl.

The di-methyl obtained from iodide of methyl and zinc by this process, and purified by fuming sulphuric acid and caustic potash, was treated with chlorine, as in the previous case, whereby a liquid was condensed which began to boil at 11°C ., and rose above 80°C . The quantity obtained was, however, but small, in consequence, no doubt, of the presence of marsh-gas from zinc-methyl which was carried over; and as it became apparent that considerable difficulty would be encountered in preparing large quantities of the pure gas, this method was abandoned.

To substitute mercury for the solution of salt would not be desirable, as the mass of mercury then required would be unmanageable.

That pure di-methyl is obtainable by this method is clearly shown by the following analysis; this gas was, however, collected in a mercury gas holder, as described in Bunsen's Gasometry.

The following analysis of di-methyl thus prepared was made according to Bunsen's method:—

	Volume.	Pressure.	Temp. C.	Vol. at 0° C. and 1m. Pressure.
Original volume of gas (moist) ..	145·62	0·1205	11·0	16·71
After addition of oxygen (moist)..	233·87	0·2563	11·8	69·74
„ „ air (moist).....	539·23	0·5075	11·8	262·3
„ explosion (moist).....	495·06	0·4637	11·5	220·3
„ absorption of carbonic acid (dry)	456·53	0·4268	11·9	186·8
„ addition of hydrogen (dry) ..	579·12	0·5461	13·2	301·8
„ explosion (dry).....	476·92	0·4351	11·4	199·4

	Found.	Calculated.
Gas employed	16·71	—
Contraction	42·30	41·77
Carbonic acid.....	33·50	33·42

III. PREPARATION OF DI-METHYL BY ELECTROLYSIS OF AN ALKALINE ACETATE.

I prepared the di-methyl by the electrolytic decomposition of acetate of potash, according to the process described by Kolbe. The gas, evolved from a platinum plate contained in a porous cell, was passed, first through a solution of caustic potash, to absorb the carbonic acid, afterwards through Nordhausen acid, and over pumice-stone moistened with oil of vitriol, to free it from a trace of oxide of methyl or hydrocarbon absorbable by this acid, and finally through a solution of caustic potash, to absorb acid fumes, any carbonic acid which had escaped the first wash bottle, or traces of sulphurous acid. The gas thus prepared had a very slight odour, and burnt with a non-luminous flame.

The following analysis of di-methyl was made according to Bunsen's method:—

	Volume.	Pressure.	Temp. C.	Vol. at 0° C. and 1m. Pressure.
(1) Original vol. of gas (moist) ..	183·48	0·1402	8·5	24·94
(2) After add. of oxygen „ ..	333·41	0·3919	8·0	127·00
(3) „ „ air „ ..	567·52	0·5221	8·5	287·5
(4) „ explosion „ ..	505·38	0·4591	9·2	224·7
(5) „ absorption of carbonic acid (dry)	447·58	0·4156	12·3	173·9

Contraction observed ..	62·80 ..	calculated for C_2H_6 ..	62·35
Carbonic acid ..	50·80 ..	„ „ ..	49·83

On similar treatment with chlorine as in the previous cases, and subsequent displacement with warm water into a receiver containing pieces of potash and surrounded by a freezing mixture of salt and ice, a colourless volatile liquid was condensed in the tube. If the gas or the chlorine was not pure, being mixed with air, very little or no liquid was condensed, being carried off by the current. The same fact was noticed by Mr. Schorlemmer. This will probably account for Frankland's observation that no liquid was condensed at $-18^{\circ}C$.

One hundred grammes of chloride were prepared by the repetition of this process. This first product was separated by distillation into two parts, one which distilled below $30^{\circ}C$., and the other above $30^{\circ}C$. On still further fractionating the first distillate, a portion was obtained boiling at $11-13^{\circ}C$., whose specific gravity was 0·9253 at $0^{\circ}C$. Pierre found the specific gravity of ethyl chloride to be 0·9241 at the same temperature.

The chloride boiling below $30^{\circ}C$. gave, on heating in sealed tubes with acetate of potash and glacial acetic acid to a temperature of $130-140^{\circ}C$. for three or four hours, a volatile fragrant liquid, having the characteristic odour of acetic ether, which, after drying over chloride of calcium and magnesia, boiled at $74\cdot0-75\cdot5^{\circ}C$. Kopp gives the boiling point of ethyl acetate at $74\cdot3$ under a pressure of 760 mm. of mercury.

In order to prepare the alcohol, the acetate was heated with crystals of baryta hydrate in sealed tubes for one or two hours, to a temperature of $120^{\circ}C$. After cooling, the liquid was distilled, and the distillate treated with dry carbonate of potash until it separated into two layers; and the upper one was decanted upon fused carbonate and afterwards upon anhydrous baryta, from which it was distilled, when it had assumed a light amber colour. It began to boil at $78\cdot1^{\circ}$, the whole coming over before the temperature exceeded $79\cdot0^{\circ}C$. Kopp gives the boiling point of ethyl alcohol prepared by fermentation at $78\cdot4^{\circ}C$. under a pressure of 760 mm. mercury, and the specific gravity at $0^{\circ}C$., as 0·8095; calculating by means of his coefficient of expansion, the specific gravity at $6^{\circ}C$. would be 0·80446, whilst I found the same to be 0·80302 at the same temperature.

The alcohol thus prepared had very little odour, agreeing in

this respect with the observation of Mendelejeff* though the specific gravity is slightly higher than his at the same temperature, calculated from his coefficient of expansion, viz., 0·80123.

On submitting this liquid to combustion analysis, the following numbers were obtained:—

No. 1. 0·2834 grm. of liquid gave 0·5357 grm. of carbonic acid, and 0·3314 grm. of water.

No. 2. 0·5533 grm. of liquid gave 1·0481 grm. of carbonic acid, and 0·6480 grm. of water.

	Percentage			Calculated from the formula C_2H_6O .	
	No. 1.		No. 2.		
C ..	51·56		51·65		52·17
H ..	12·99		13·02		13·04
O ..	35·45		35·33		34·79
	<hr/> 100·00		<hr/> 100·00		<hr/> 100·00

The numbers are not all that could be desired when compared with the calculated composition; this is, however, owing to the difficulty in burning so volatile a liquid, and to the small quantities taken. Dumas and Boullay† state that, in order to obtain accordant results upwards of a grm. of liquid was necessary; in one combustion 1·742 grms. was used; with ether a still greater quantity was required.

The alcohol still remaining in the carbonate of potash and in the dilute solution was separated by distillation; this distillate was oxidized by a mixture of bichromate of potash and sulphuric acid, when the characteristic odour of aldehyde was recognised; and the oxidation was continued until it had disappeared. On distilling to dryness, an acid distillate was obtained: this was neutralized with pure carbonate of soda, and yielded on evaporation needle-shaped crystals of acetate of soda. The mother-liquor was distilled to dryness with sulphuric acid; and the distillate was neutralized with pure carbonate of silver, and filtered boiling. On cooling it yielded colourless transparent flat needles, which, after drying over sulphuric acid, gave on analysis the following numbers:—

No. 1. 0·4142 grm. of salt gave 0·2663 grm. of metallic silver.

* Zeitschrift für Chemie, 1865, p. 257.

† Ann. Ch. Phys., 1827 [3], xxxvi, 299.

No. 2. 0.5095 grm. of salt gave 0.3274 grm. of metallic silver.

No. 3. 0.3650 grm. of salt gave, after drying at 100° C. in a water-bath for one hour, 0.2349 grm. of metallic silver.

No. 4. 0.2483 grm. of salt gave, after drying at 100° C. in a water-bath for two days, 0.1604 grm. of metallic silver.

Estimation No. 1 gave 64.30 per cent. of silver.

"	2	"	64.25	"
"	3	"	64.36	"
"	4	"	64.60	"

Calculated from the formula $\left. \begin{matrix} \text{C}_2\text{H}_3\text{O} \\ \text{Ag.} \end{matrix} \right\} \text{O, acetate of silver yields}$
64.68 per cent. of silver.

That portion of the mixed chlorides which distilled above 30° C. was fractionated, when two-thirds of the total volume distilled over between 57°—59° C., and consist, as the following analyses prove, of the monochlorinated chloride of ethyl. The specific gravity of this liquid was found to be 1.198 at 6.5° C. Regnault found the sp. gr. to be 1.174 at 17° C., and the boiling point to be 64° C.*

Beilstein† has shown that mono-chlorinated ethyl chloride, and chloride of ethylidene obtained by acting on aldehyde with perchloride of phosphorus, are identical; the boiling point of the latter, as observed by Wurtz, is 58–59°, and the specific gravity, as determined by Geuther, is 1.189 at 4.3° C.;—these numbers agree with those I found. Beilstein remarks that the higher boiling point, as observed by Regnault, would result from the presence of more highly chlorinated products.

The following numbers were obtained by analysis:—

No. 1. 0.5206 grm. gave 0.3691 grm. of chlorine.

No. 2. 0.4491 " " 0.3186 "

No. 3. 0.4292 " " after drying over solid caustic potash for a week, 0.3010 grm. of chlorine.

Percentage of chlorine found by No. 1, 70.89

"	"	"	2, 70.94
"	"	"	3, 71.76

* Ann. Ch. Phys. [2], lxxi, 355.

† Ann. Ch. Pharm., cxiii, 110.

The percentage required by the formula of monochlorinated ethyl chloride $\left. \begin{matrix} \text{C}_2\text{H}_4\text{Cl} \\ \text{Cl} \end{matrix} \right\}$ is 71.73.

Hence the mono-chlorinated ethyl chloride was formed in quantity by the action of excess of chlorine on di-methyl.

The foregoing results confirm the conclusion that only one hydrocarbon, C_2H_6 , exists, and that this substance, from whatever source it may be prepared, always yields ethyl chloride when treated with chlorine.