VII.—*Action of Phosphorus Pentachloride on Ethylic Diethylacetoacetate.*

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THE action of phosphorus pentachloride on ethylic acetoacetate was first carefully investigated by Geuther (*Jenaische Zeitschrift*, **4**, Heft 4), who found that the ethoxyl-group was displaced by chlorine, giving rise to the chlorides of two isomeric chlorocrotonic acids.

Some years later, Rücker (*Annalen*, **201**, 56) submitted an ethereal monalkylacetoacetate to the same treatment, and again found that the ethoxyl of the carboxyl-group was displaced by chlorine, the product being the chloride of a single monalkylchlorocrotonic acid. Judging from these results, it was to be expected that the action of phosphorus pentachloride on a dialkylacetoacetate would give rise to the formation of the chloride of a dialkylchlorocrotonic acid; this, however, is not the case, the chief result of the reaction being a mono-, and a di-chloro-*substitution product*, together with a small quantity of a monalkylchlorocrotonic ethylic salt, as the following experimental results testify.

100 grams (1 mol.) of ethylic diethylacetoacetate boiling at 205—215° was poured into a flask containing 225 grams of phosphorus pentachloride (2 mols.). No reaction took place at the ordinary temperature or at 100°; the mixture was therefore gently heated in connection with a reflux condenser until all the chloride had dissolved, and was kept boiling gently for some time. The upper end of the condenser contained a calcium chloride tube, which entered a cylinder filled half full of water. A thermometer placed in the vapour of the boiling liquid remained very constant at 85°, so the temperature in the liquid could hardly have been much over 100°. During the reaction, volumes of hydrogen chloride were evolved, and also some ethyl chloride which could be inflamed in the cylinder. After boiling for five hours, the liquid had become pale yellow, and on cooling about 25 grams of unused phosphorus pentachloride crystallised out. The liquid poured off from the crystals was now distilled until the thermometer showed 120°, in order to remove most of the phosphorus oxychloride and trichloride, of which it mainly consisted. The residue, which was now brown in colour, was allowed to cool and poured into cold water; and then, as it could not be boiled under ordinary pressure without undergoing considerable decomposition, it was distilled in a current of steam. The oil which passed over very slowly was heavier than water, and insoluble in it. It was collected in three principal fractions of equal volume (I, II, III). The first drops which distilled possessed a peculiar odour, resembling that of the camphor compounds; this was collected separately, but owing to the small quantity it has not been more closely examined; it boils below 200°, with slight decomposition. The last portion was also collected apart (about 3 c.c., Fraction IV). Each of the above fractions was separated from the water, dried over sulphuric acid, and afterwards analysed.

The aqueous distillate had a strongly acid reaction, but after neutralising with sodium carbonate, evaporating to dryness and exhausting with absolute alcohol, only a small quantity was dissolved, the residue consisting of sodium chloride. The liquid in the flask

also had a strongly acid reaction due to phosphoric and phosphorous acids.

Fraction I.—A portion (a) of this slightly yellowish liquid, on distillation, boiled from 210° to 220° with decomposition, hydrogen chloride being given off whilst a dark-brown residue remained in the retort. This distillate was analysed, as was also another portion which had not been distilled (b).

(a). 0.2685 gram substance produced 0.550 gram CO_2 and 0.2025 gram H_2O .

0.2195 gram heated with CaO gave 0.118 gram AgCl .

(b). 0.255 gram substance gave 0.517 gram CO_2 and 0.187 gram H_2O .
0.3145 gram finally produced 0.195 gram AgCl .

	Calculated for $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{C}(\text{C}_2\text{H}_5)_2\cdot\text{COOC}_2\text{H}_5$.		Found.	
			a.	b.
C_{10}	120	54.42	55.86	55.3
H_{17}	17	7.72	8.3	8.14
O_3	48	21.77	—	—
Cl	35.5	16.09	13.3	15.32
	<hr/> 220.5	<hr/> 100.00		

The substance, according to these analyses, consisted mainly of ethylic diethylmonochloracetoacetate slightly contaminated with a compound richer in carbon and hydrogen, probably free from chlorine.

Ethylic diethylchloracetoacetate is a colourless liquid, insoluble in water, and of a pleasant odour. It has a sp. gr. of 1.063 at 15° . It is miscible in all proportions with alcohol, ether, and benzene.

Fraction II.—This might consist of a mixture of the two substances which composed fractions I and III, that is, a mixture of mono- and di-chlorinated ethylic diethylacetoacetate, but also of ethylic ethylchlorcrotonate, $\text{CH}_3\cdot\text{CCl}:\text{C}(\text{C}_2\text{H}_5)\cdot\text{COOC}_2\text{H}_5$.

Two chlorine estimations, in two samples separately prepared, gave 21.8 and 21.1 per cent. Cl , which agree pretty well with the amount of chlorine in this last-named ether, but also equally consistently for a mixture of equal numbers of molecules of mono- and di-chlorinated ethylic diethylacetoacetate.

This fraction was consequently again distilled in a current of steam until one-half had passed over, dried over sulphuric acid, and the chlorine determined.

Fraction IIa.

0.288 gram substance produced 0.200 gram AgCl = 17.1 per cent. Cl .

Fraction IIb.

0.277 gram substance produced 0.265 gram AgCl = 23.6 per cent. Cl.

Calculated for ethylic diethylmonochloracetoacetate 16.1 per cent.

Calculated for ethylic diethyldichloracetoacetate 27.8 per cent.

Presuming that fractional distillation in a current of steam can be carried out with a fair amount of exactitude,* these results tend to show that a compound was present which was neither the monochloro- nor dichloro-substitution product, since in the first case the chlorine found would be too high, and in the second too low. I have substantiated this supposition by again distilling Fraction IIb to one-half, and analysing it.

Fraction IIb 1.

0.3245 gram substance produced 0.266 gram AgCl = 20.2 per cent. Cl.

0.3140 gram substance produced 0.6200 gram CO₂ and 0.2005 gram H₂O.

	Calculated for $\text{CH}_3\cdot\text{CCl}\cdot\text{C}(\text{C}_2\text{H}_5)\cdot\text{COOC}_2\text{H}_5$.		Found.	
			I.	II.
C ₈	96	54.4	—	53.85
H ₁₃	13	7.36	—	7.09
O ₂	32	—	—	—
Cl	35.5	20.11	20.2	—
	<hr/> 176.5			

Although the percentage of chlorine found agrees with the above formula, still the carbon, and especially the hydrogen, are too low. It is, I think, extremely probable that this substance consists mainly of pure ethylic ethylechlorcrotonate, as the evolution of ethyl chloride and the occurrence of phosphorus oxychloride can then be satisfactorily accounted for.

Fraction III.—Analyses have shown this fraction to be a dichloro-substitution product of ethylic diethylacetoacetate.

I. 0.274 gram substance produced 0.297 gram AgCl.

II. 0.3135 " " " 0.5455 gram CO₂ and 0.182 gram H₂O.

The oil was now distilled to one-half, and that remaining in the flask dried and analysed for chlorine. The percentage was found to be nearly the same.

* In these operations a long-necked flask was used, and the tube in connection with the condenser was about $\frac{1}{8}$ in. in diameter.

III. 0.2775 gram substance gave 0.319 gram AgCl.

	Calculated for		Found.		
	$\text{CHCl}_2 \cdot \text{CO} \cdot \text{C}(\text{C}_2\text{H}_5)_2 \cdot \text{COOC}_2\text{H}_5$		I.	II.	III.
C_{10}	120	47.05	—	47.4	—
H_{16}	16	6.27	—	6.4	—
O_3	48	—	—	—	—
Cl_2	71	27.84	26.8	—	28.4
	—	255			

Ethyl diethyldichloroacetate is an oily, slightly yellow liquid, having a pleasant odour. It is insoluble in water, but miscible with alcohol and ether, and has at 15° a sp. gr. of 1.155. It cannot be distilled under the ordinary pressure.

Fraction IV.—This liquid, consisting of the last drops which were distilled, appears to contain about 50 per cent. of a trichloro-substitution product of ethyl diethylacetate, the percentage of chlorine in which is 36.8.

0.2115 gram produced 0.2655 gram AgCl = 31.06 per cent. Cl.

II. Formation of Oxyketones—Action of Sodium Methylate on Ethyl Diethylchloroacetate.

A solution of 4.2 grams of sodium (1 mol.) in 40 grams of methyl alcohol was poured into 40 grams of ethyl diethylmonochloroacetate* contained in a flask; a reaction took place at once with considerable elevation of temperature, the liquid becoming brown. It was necessary to place the flask in cold water for a time, but afterwards the mixture was heated on the water-bath, and finally in sealed tubes for three hours at 100°. The contents of the tubes were then distilled to dryness on an oil-bath, and the distillate fractionated. Most of the methyl alcohol was thus separated, and the residue, which boiled from about 80° upwards, was shaken with a saturated solution of calcium chloride several times, and the upper layer separated and submitted to fractional distillation. From this liquid, I succeeded in obtaining two compounds; one boiled at 130—132° and represented the principal part, the other passed over between 185—190° and was obtained only in small quantity.

An analysis of the liquid boiling at 185—190°, which still contained a little chlorine, gave the following numbers:—

* Obtained from 100 grams of diethylacetate and PCl_5 . After distilling 1 or 2 c.c. in a current of steam, the remainder was collected until about two-fifths of the whole had passed over.

0.2265 gram substance produced 0.5135 gram CO_2 and 0.1855 gram H_2O .

	Calculated for $\text{C}_{11}\text{H}_{20}\text{O}_4$.		Found.
	132	61.11	
C_{11}	132	61.11	61.82
H_{20}	20	9.21	9.09
O_4	64	29.68	—
	216	100.00	

This result agrees in the main with the composition of ethylic methoxydiethylacetoacetate, $\text{CH}_2(\text{OCH}_3) \cdot \text{CO} \cdot \text{C}(\text{C}_2\text{H}_5)_2 \cdot \text{COOC}_2\text{H}_5$. It is a pleasant smelling, colourless liquid, soluble in alcohol and ether, and heavier than water, in which it is insoluble.

I have not been able to obtain this compound free from chlorine. If an excess of sodium methylate is taken, in order to remove the whole of the chlorine, the substance boiling from 130 — 132° is chiefly produced.

Analysis of the body boiling from 130 — 132° :—

- I. 0.276 gram substance gave 0.6475 gram CO_2 and 0.268 gram H_2O .
- II. 0.2745 gram substance, obtained from a second preparation, gave 0.6465 gram CO_2 and 0.2725 gram H_2O .
- III. 0.2465 gram of the same substance gave 0.5820 gram CO_2 and 0.2415 gram H_2O .
- IV. 0.320 gram of the portion boiling from 125 — 130° , which was very little, gave 0.7600 gram CO_2 and 0.317 gram H_2O .

	Calculated for $\text{C}_7\text{H}_{14}\text{O}_2$.		Found.			
	84	64.6	I.	II.	III.	IV.
C_7	84	64.6	64.0	64.2	64.4	64.7
H_{14}	14	10.8	10.78	11.03	10.84	11.0
O_2	32	24.6	—	—	—	—
	130	100.0				

These numbers agree pretty well with each other, and with the formula of an oxyketone, viz., methoxymethyl-ethyl-acetone (*methoxy-methyl butyl ketone*), $\text{CH}_2(\text{OCH}_3) \cdot \text{CO} \cdot \text{CH}(\text{CH}_3)(\text{C}_2\text{H}_5)$. It might certainly have been expected that a methoxy-diethyl-acetone would have been formed, according to the following equations :—

But this, according to the analytical results, does not appear to be the case. The place of one ethyl-group has been taken by methyl, and this displacement is probably brought about by the excess of methyl alcohol. The researches of Geuther and Bachmann (*Annalen*, **218**, 49) have already shown that in the case of the ketals (and this oxyketone is possibly nearly related to them) a positive organic radicle can be displaced by another *poorer in carbon*, e.g., by the action of methyl alcohol on diethylacetal, methylethylacetal and dimethylacetal are formed.

Methoxymethyl-ethyl-acetone is a mobile, colourless liquid, of sp. gr. 0.855 at 20°, very much resembling acetal. It has a burning taste and a very pleasant odour, and it can be mixed with alcohol and ether, but is insoluble in water. It boils at 130—132°, and the vapour burns with a luminous flame tinged with blue. No compound with sodium hydrogen sulphite could be obtained.

Action of Sodium Methylate on Ethylic Diethyldichloroacetoacetate.

A solution of 9.5 grams of sodium (2 mols.) in 70 grams of methyl alcohol was poured into a flask containing 50 grams of pure ethylic diethyldichloroacetoacetate, and the mixture treated precisely as before described. In this case also, I finally obtained two liquids boiling at 134—135° and 190—200°; this last portion was very little, and consisted chiefly of ethylic dimethoxydiethylacetoacetate, as the following analysis shows:—

0.211 gram substance gave 0.4445 gram CO₂ and 0.165 gram H₂O.

	Calculated for C ₁₂ H ₂₂ O ₅ .		Found.
C ₁₂	144	58.53	57.4
H ₂₂	22	8.94	8.7
O ₅	80	32.53	—
	246	100.00	

I have endeavoured, in vain, to obtain this substance in a purer state; it always contains a little chlorine, and since it is slightly decomposed by distillation, the chlorine compound cannot be got rid of in this way. An excess of sodium methylate causes a further decomposition, as in the case of the monochlorinated derivative.

Ethylic dimethoxydiethylacetoacetate,

is a pleasant smelling, colourless liquid, heavier than water, in which it is insoluble; it boils with partial decomposition about 195° .

An analysis of the substance boiling at 134 — 135° gave the following result:—

- I. 0.3235 gram substance gave 0.7335 gram CO_2 and 0.3065 gram H_2O .
 II. 0.239 gram substance gave 0.5455 gram CO_2 and 0.225 gram H_2O .

	Calculated for $\text{C}_9\text{H}_{13}\text{O}_3$		Found.	
			I.	II.
C_9	108	62.06	61.83	62.24
H_{13}	18	10.34	10.52	10.46
O_3	48	27.60	—	—
	174	100.00		

These numbers correspond very closely with the above formula, which represents a *dimethoxy-diethyl-acetone*,

The following equations explain its formation:—

It is a colourless, mobile, pleasant smelling liquid, having a burning taste. It boils at 134° , and has a sp. gr. of 0.886 at 15° . It is insoluble in water, but miscible with alcohol and ether in all proportions. Its vapour burns with a luminous flame. No compounds are formed with acetic anhydride or sodium hydrogen sulphite.

The yield of these two methoxyketones is by no means a good one; this is chiefly because a considerable quantity passes over with the methyl alcohol, and cannot be separated by fractional distillation; still, by adding powdered calcium chloride to the methyl alcohol distillate until a syrup is formed, shaking with ether—which dissolves the oxyketones—and then removing the ether on a water-bath at 50° , I have succeeded in recovering a fair amount of these compounds.

I am not aware that a methoxyketone has been previously described, although L. Henry has recently (*Ber.*, **14**, 2272) prepared the

ethyl salt of the alcohol of pyrroacemic acid, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OC}_2\text{H}_5$, which he obtained from propargyl ether by means of mercuric bromide and water.

Ammonia and Ethylic Diethylacetoacetate.

By the action of concentrated aqueous ammonia on this substance, it was expected that amides would be obtained analogous to those produced from ethylic acetoacetate, at the same time its abnormal reaction with phosphorus pentachloride seemed to predict failure, and this prediction has been verified by experiment. No reaction takes place at $120\text{--}130^\circ$ in sealed tubes, and on heating still higher, finally to $190\text{--}200^\circ$, the ethylic diethylacetoacetate becomes decomposed, forming ammonium carbonate and diethylacetone boiling at $135\text{--}137^\circ$.