PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XII.—On *Ethyl-amyl*.

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ETHYL-AMYL was first prepared by Wurtz (*Ann. Ch. Phys.* [3], liv, 278), who formed it by the action of sodium on the iodides of ethyl and amyl. He found its boiling point to be 88° , and its specific gravity 0.7069, but did not study any of its derivatives. In 1862 (*Journ. Chem. Soc.* [2], i, 425), Schorlemmer showed that by the action of chlorine it yielded a heptyl chloride, and in 1866 (*Proc. Roy. Soc.*, xiv, 168), he investigated other derivatives of this hydrocarbon, and prepared its acetate and alcohol, from the latter of which he obtained by oxidation an acid having the composition of cœnanthylic acid. In a further communication to the Royal Society, he proved that the hydrocarbon heptane boiling at 99° , is not identical with ethyl-amyl.

We now know the cause of this isomerism, for Schlorlemmer has shown that the heptane from petroleum is a normal paraffin having the constitution—

whilst from the constitution of amyl alcohol (Erlenmeyer, *Ann. Chem. Pharm. Suppl.* v, 337), it follows that ethyl-amyl contains the group isopropyl, its constitution being—

By his recent researches on the normal paraffins (*Trans. Roy. Soc.* clxii, p. 111), Schorlemmer has further shown that, by acting with chlorine on these hydrocarbons, in addition to a primary, a secondary chloride is formed. It appeared therefore of great interest to study the action of chlorine on the other paraffins not belonging to the normal group, whose constitution is well known, and to examine carefully the oxidation-products of the alcohol derived from them.

Of these, ethyl-amyl is for obvious reasons the most suitable, and at the request of Mr. Schorlemmer I undertook an investigation of this hydrocarbon in the sense above indicated.

The high price of iodine at the time rendered it advisable to endeavour to prepare ethyl-amyl from the bromides instead of the iodides, and on experiment the yield of hydrocarbon, allowing for loss owing to the volatility of the ethyl bromide, was found to be satisfactory. The total quantity obtained was about a litre and a half.

To prepare the amyl bromide, 400 grams of amyl alcohol and 25 grams of amorphous phosphorus were placed in a tubulated retort or a flask connected with an inverted condenser. 350 grams of bromine placed in a stopcock-funnel was then gradually added, and the mixture allowed to stand over night. The liquid was then poured off from the undissolved phosphorus, if any, and distilled into a receiver containing a solution of caustic soda. The bromide was shaken up with caustic soda solution, and then with water, afterwards dried with sticks of caustic potash, and subjected to fractional distillation, the portion boiling between 118° , and 124° , being taken to prepare the ethyl-amyl. The average yield of bromide was about 600 grams, from 400 alcohol and 350 of bromine.

The ethyl bromide was prepared in the same way, the proportions taken being 450 grams of methylated alcohol once distilled, 400 grams of bromine and 40 grams of amorphous phosphorus, care being taken to keep the mass cool. Almost the whole of the bromide thus obtained on distillation from the water bath, boiled constantly at 41° .

In order to prepare the ethyl-amyl, 150 grams each of the ethyl and amyl bromides and about 50 grams of sodium were taken (there being somewhat more than an equivalent quantity of the ethyl bromide, to allow for loss owing to its greater volatility). The mixed bromides were placed in a flask connected with a long, well cooled, inverted condenser.

The sodium was added gradually so as to keep the temperature at about 20° to 25° C., which object is aided by placing the flask in an oil-bath, and surrounding this if necessary with a vessel of water. It is necessary to be particular about this point, as below this temperature scarcely any action takes place, whilst at higher temperatures the action is so violent as to occasion a loss of material; still when the action does not readily commence, as is sometimes the case, a little heat may be applied without any danger, provided there be not much sodium present. When all the sodium had been added, and all action had ceased, heat was applied to the oil-bath, and the temperature kept at about 100° for some hours, so that the liquid dropped back pretty rapidly from the inverted condenser. The condenser was then reversed and the products of the reaction distilled off. The average yield of hydrocarbons from 150 grams of amyl bromide and 150 grams of ethyl bromide was about 100 grams, consisting of 80 grams ethyl-amyl and 20 grams diamyl. However large the excess of ethyl bromide, there

was always some diamyl formed, the quantity of which varied greatly with the same proportions of the bromides, 150 grams of each, giving in one case 30 grams of diamyl and 77 grams of ethyl-amyl, and in another only 8 grams of diamyl to 92 grams of ethyl-amyl. The circumstances under which the di-amyl was formed could not be ascertained, as neither the temperature at which the reaction was carried on, nor the length of time which it occupied, was found to determine the formation. There was always also a certain quantity of ethyl bromide left undecomposed.

After having been distilled off, the mixture of hydrocarbons was allowed to stand for some weeks over sodium. It was then repeatedly rectified over sodium, and fractionally distilled. The portions boiling from 85° to 100° were then treated with strong sulphuric and nitric acids.

By the usual method of adding strong sulphuric acid and then nitric acid by degrees, it takes almost a week before all action ceases, but by proceeding as follows the action is finished in a much shorter time. About one quarter of its volume of strong sulphuric acid is added to the hydrocarbon, and allowed to stand for a few hours, with frequent agitation. The acid is then drawn off by a separating funnel, and is found to contain all the impurities, as on addition of fresh sulphuric acid and a little nitric acid, hardly any action takes place, and altogether ceases if the mixture be allowed to stand overnight.

After separation from the acids, the hydrocarbon was washed twice with about its own volume of water, and left in contact with sticks of caustic potash for forty-eight hours, after which it was again fractionally distilled with a little sodium, when all except a very small portion came over from 88° to 90° . In order to obtain the hydrocarbon as pure as possible, the portion remaining after it had been repeatedly treated with chlorine, was left in contact for a week or two with sticks of caustic potash. On distillation, the ethyl-amyl thus obtained was found to have a constant boiling-point of 90° . The following is the analysis:—

0.1746 grams ethyl-amyl gave 0.5402 grams CO_2 , and 0.2460 grams H_2O .

	Percentage.	
	Calculated.	Found.
C_7	84	84.37
H_{16}	16	15.66

Specific gravity—

Weight of bottle and ethyl-amyl at 18.4°	(1)	4.4465
”	”	(2) 4.4468
”	”	(3) 4.4464
		z 2

Weight of bottle and water at 18°	5.1065
Weight of bottle	3.0227

which gives the specific gravity at 18.4° of 0.6833.

In order to effect the chlorination of the ethyl-amyl, about 100 grams of the hydrocarbon were placed in a flask into which chlorine, dried by sulphuric acid, was led by a tube reaching down in the flask to within about 90 millimeters of the surface of the liquid. The flask was connected with an inverted condenser, at the upper end of which were placed two washing bottles containing solution of caustic potash, to arrest any hydrocarbon that might be carried over. The chlorine was allowed to pass through the apparatus until all the air was driven out; the hydrocarbon was then placed in the flask and heat applied so as to allow the liquid to drop quickly back from the condenser.

This was continued for the whole of the day; the flask was then removed, and the unattacked hydrocarbon separated from the chlorinated products by very slow fractional distillation, another portion of the hydrocarbon being in the meanwhile subjected to the action of the chlorine.

It was found necessary, when the day was at all bright, to protect the flask from the action of the light, as the chlorine took fire and burned in the vapour of the hydrocarbon. This also took place when the light was not so strong, if the current of chlorine were allowed to pass too rapidly.

The chloride thus obtained was subjected to several fractional distillations, and the portion boiling between 140° and 150° (which formed nearly the whole quantity) was taken to prepare the acetate. It was, however, found that small quantities of more highly chlorinated products were always formed during the reaction.

The following is the analysis of the chloride thus obtained:—

- (1.) 0.227 grm. chloride gave 0.221 AgCl and 0.028 Ag.
 (2.) 0.5205 „ „ 0.5503 „ 0.0219 „

Calculated for $C_7H_{15}Cl$.	Found.	
	(1)	(2)
26.39 p. c. Cl.	25.7	26.15

For the preparation of the acetate, about 15 or 20 grams of the chloride, with rather less than that quantity of potassium acetate and of glacial acetic acid, were inclosed in strong glass tubes of about 25 millimeters in diameter, and heated to 200° for about six hours, or until the reaction was completed, this being shown by the ceasing of the separation of potassium chloride at the juncture of the two layers of liquid. That all the chlorine was removed was shown by burning a little of the inflammable liquid, the flame of which showed not the slightest tinge of green.

0.1547 of the acetate gave 0.3850 of CO_2 and 0.157 H_2O .

The lower-boiling liquid from the acetate (that boiling from 85° to 100°) was allowed to stand over caustic potash, and on fractional distillation, yielded heptylene having a constant boiling-point of 91° C., and a specific gravity of 0.706 at 16° C., from the following numbers:—

To prepare the alcohol, enough ethyl alcohol was added to the acetate to make a clear liquid, and then an excess of caustic potash, and the whole was allowed to stand for twenty-four hours with frequent shakings. To remove the last traces of acetate, the liquid was gently heated for an hour or two with a stick of caustic potash, until the odour of the acetate had entirely disappeared. The alcohol was then washed twice with water, dried over ignited potassium carbonate, and fractionally distilled. The distillation commenced at 145° , and the highest point reached was 170° . The lowest portion was again washed to remove traces of ethyl alcohol.

As the quantity of alcohols was small, the separation could not have been complete, though it was sufficiently so to show the existence in

the liquid of the two alcohols having a considerable difference in their boiling-points. The two portions were therefore placed together for oxidation, as the different nature of the products of this oxidation would allow of a very complete separation one from the other.

For the same reasons a portion of the "mixture" of the two alcohols was taken for analysis, which yielded the following results:—

0·2142 grams of alcohol gave 0·5664 grams CO_2 and 0·2666 grams H_2O .

		Percentage.	
		Calculated.	Found.
C_7	84	72·4	72·11
H_{16}	16	13·8	13·83
O	16	13·8	—
	<hr/> 116	<hr/> 100·0	

Oxidation of the Alcohols.

The mixture of the alcohols was subjected to the action of an oxidising mixture of 3 parts strong sulphuric acid, 2 parts potassium bichromate, and 10 parts water (Schorlemmer, *Proc. Roy. Soc.*, cxiv, 125). The mixture was allowed to become quite cold, and added to the alcohol in small quantities at a time, any elevation of temperature being avoided by placing the containing vessel in cold water. The liquid was frequently shaken, and the oxidising mixture added until a permanent brown tinge showed that there was an excess. It was allowed to stand overnight and then distilled in a retort until most of the liquid portion had come over, the distillate consisting of an acid liquid on which floated an oily layer. The residue in the retort was filled up to the original bulk and again distilled. This was repeated once more, and then all the distillates were neutralised with sodium carbonate and distilled in a retort until all the oily liquid had come over. The residue was evaporated down to dryness on the water-bath, forming a crude sodium salt of the acid.

The crude sodium salt was decomposed by the minimum quantity of dilute sulphuric acid, and the oily acid thus formed was separated by a funnel and dried for a day or two over phosphorus pentoxide. Its boiling-point was found to be 210° to 213° (not corrected). It was a colourless oily liquid, lighter than water, possessing a peculiar and disagreeable odour.

Preparation of salts of the acid—

(1.) *Silver Salt*.—The portion of the acid which was left mixed with the phosphorus pentoxide, was diluted with a considerable quantity of water and distilled in a retort, the distillate forming an acid liquid

with a little of the undissolved acid floating on the top. This distillate was heated to boiling and carbonate of silver added until the liquid was only slightly acid; the solution was filtered whilst hot, and on cooling, the silver-salt separated out as a white precipitate, sometimes granular and sometimes flocculent. On being left to crystallise by spontaneous evaporation, the salt was obtained in minute needle-shaped crystals. The precipitate was dried by pressure between blotting-paper and then placed over sulphuric acid for twenty-four hours. In determining the silver, the salt was placed in a porcelain crucible and heated very gradually; it first melted to a dark liquid having a green metallic lustre, at the same time decomposing. The heat was increased until all the organic matter was driven off, and the residual silver heated to fusion over the blowpipe. The following is the analysis—

(1.) 0.101 Ag salt gave 0.0463 Ag.

(2.) 0.035 ,, 0.0160 ,,

Calculated for $C_7H_{13}AgO_2$. 45.57 p. c. Ag.	Found.	
	(1)	(2)
	45.84	45.71

(2.) *Barium Salt*.—A portion of the acid was boiled with a little water and nearly neutralised with barium carbonate. Neither on evaporation by heat nor over sulphuric acid could this salt be obtained in any form but as a gummy skin; and though on leaving the solution at rest for several weeks, it separated out in what seemed to be a crystalline form, the salt on analysis showed no definite composition.

(3.) *Calcium Salt*.—The barium salt was decomposed by dilute sulphuric acid and the acid distilled off. The boiling solution of this was nearly neutralised with milk of lime, filtered, and allowed to evaporate at a gentle heat. The salt was thus obtained crystallised in microscopic plates and needles, which after drying between blotting-paper, lost on heating to 160° , 9.35 per cent. of moisture, corresponding most nearly with $Ca(C_7H_{13}O_2)_2 + 2Aq$, which requires 10.78 per cent.

The following is the analysis of the salt:—

0.0652 of the salt, lost on heating to 160° , 0.0061, and the resulting 0.0591 of the dry substance gave 0.0205 of $CaCO_3$.

Calculated for $Ca(C_7H_{13}O_2)_2$. 13.42 p. c. of Ca.	Found.
	13.87

The distillate from the sodium salt, containing the oily liquid was again distilled as long as oil came over, and this was repeated twice. The last distillate was saturated with potassium carbonate to bring as much of the liquid out of solution as possible. The light layer of liquid was separated and dried over fused potassium carbonate. On

The liquid boiling at 144° is colourless, has a faint fruity smell, and forms a crystalline compound with sodium bisulphite, which proves it to be an acetone.

Weight of bottle and acetone at 17°	(1)	4.8548
" " "	(2)	4.8551
" and water at 17°		5.1073
Weight of bottle		3.0220

0.2373 of substance gave 0.643 of CO_2 and 0.2655 of H_2O .

Oxidation of the Acetone.—The acetone was placed in a flask with a quantity of the chromic acid mixture, and connected with an inverted condenser; it was heated gradually to boiling, and kept in ebullition for an hour or two, when the oily layer had almost disappeared and the liquid had assumed a green tint.

The liquid and unoxidised acetone were then distilled off; the right quantity of potassium bichromate and sulphuric acid was added, and the liquid heated and distilled as before. The two residues of oxidising mixture were added together and distilled with water until no acid liquid came over. All the distillates were then neutralised with sodium carbonate, and evaporated down in a retort to separate any unoxidised acetone, and then on a water-bath to dryness. The sodium salt was decomposed by a small quantity of dilute sulphuric acid and a layer of an oily acid having the odour of valerianic acid, separated out on the surface of the acid solution. The whole was distilled in a small retort until all the oily liquid had come over, and the distillate thus obtained was distilled several times in the same way, to obtain the oily acid as free from water as possible, and to separate it from the other acid in solution. The liquid was then saturated with calcium chloride to bring as much as possible of the acid out of solution, and the upper layer of liquid separated and dried over phosphorus pentoxide. The residual calcium chloride solution was again partially distilled, the distillate saturated with more calcium chloride, and a little more

of the acid thus obtained. When rendered quite anhydrous by the phosphorus pentoxide, the acid was distilled and found to boil between 173° and 176° (not corrected).

Preparation of the Salts.

(1.) The silver salt was made in the same manner as that of the enanthylic acid, and it decomposed in the same way when heated. The following is the analysis:—

(1.) 0.050 Ag. salt, gave 0.026 of Ag.

(2.) 0.0117 " " 0.006 "

Calculated for $C_5H_9AgO_2$.	Found.	
	(1)	(2)
51.67 p. c. of Ag.	52.00	51.29

The solubility of the salt was found to be 1 part in 97.4 of water at 18° , or 100 parts water at 18° dissolve 1.03 parts, for 11.4945 grams of solution at 18° gave 0.0793 AgCl and 0.0087 Ag.

(2.) The boiling solution of the acid was nearly neutralised with barium carbonate to form the barium salt; but though the liquid was left standing for some weeks, the salt could not be obtained in a crystalline form, only a sort of skin forming on the surface. The same took place on evaporating down by heat, or over sulphuric acid.

(3.) As the barium salt would not crystallise, it was decomposed by dilute sulphuric acid, the acid distilled off, and the solution, after heating, neutralised with calcium hydrate, to form the calcium salt. On cooling, this salt separated out in small, short, colourless needles. On evaporation by heat, the salt separated out in the form of a gummy skin on the surface, but on cooling, this skin became brittle, and assumed the same crystalline form. A portion of the solution having been left for about a week in a small test-tube, the salt separated out in a beautiful, arborescent form, on the side of the tube. The salt was dried between blotting-paper, and analysed.

0.0705 grams dried at 160° , lost 0.007 grams., and gave 0.027 $CaCO_3$.

The moisture lost was 9.93 per cent., corresponding to $Ca(C_5H_9O_2)$. $1\frac{1}{2}Ag$., which contains 10.04 per cent.

Calculated for $Ca(C_5H_9O_2)_2$.	Found.
16.53 p. c. of Ca.	17.00

The residue from the valerianic acid was distilled as nearly to dryness as possible; the distillate being an aqueous liquid, having an acid reaction, and the odour and taste of acetic acid. To concentrate the acid, the liquid was repeatedly distilled to a small bulk, and the strongly

acid residues collected together. This was heated to boiling, nearly neutralised with silver carbonate, and filtered whilst hot. On cooling, the silver acetate separated out in thin, flat, colourless, shining needles. On drying between blotting-paper and over sulphuric acid, it yielded on analysis the following result:—

- (1) 0.098Ag. salt gave 0.363Ag.
 (2) 0.174 „ „ 0.112 „

Calculated for $C_2H_3AgO_2$. 64.67 p. c. Ag.	Found.	
	(1)	(2)
	64.3	64.37

From the results of these experiments the following conclusions may be drawn:—

Schorlemmer's observation of the formation of two isomeric chlorides by the action of chlorine on the normal paraffins, is evidently borne out in the case of ethyl-amyl: for a mixture of chlorides was obtained which did not give any constant boiling-point, but yet distilled almost entirely within about 10° . This mixture yielded, by the action of potassium acetate and acetic acid, a liquid which also could not be obtained of constant boiling point, but distilled within about 15° . From this, however, a mixture of alcohols was obtained, of which a more or less complete separation could be effected into one boiling at about 147° , and another boiling at 165° .

The primary alcohol obtained is an iso-heptyl alcohol. This is shown by its boiling-point, which is about 10° lower than that of the normal heptyl alcohol, which boils at 170° — 175° (Schorlemmer, *Proc. Roy. Soc.*, 1872, vol. 162, p. 121), and by the acid yielded on oxidation, which must be iso-cenanthylic acid. The boiling-point of this acid was found to be 210° — 213° , being about 8° or 10° lower than that of the normal acid, which boils at 221° (Schorlemmer, *Proc. Roy. Soc.*, clxii, 121); but as ethyl-amyl contains three methyl-groups, two isomeric primary alcohols may be derived from it, namely:—

It is for the present impossible to decide which of these two formulæ expresses the true constitution, but perhaps the second formula is the more probable.

The secondary alcohol is methyl-amyl carbinol, $\text{CH} \begin{cases} \text{OH} \\ \text{CH}_3 \\ \text{C}_3\text{H}_5(\text{CH}_3)_2 \end{cases}$.

That it has really this constitution is proved by the fact that on oxidation it yields methyl-amyl ketone, boiling at 143° — 145° , which is identical with that prepared by Popoff (*Zeitsch. f. Chemie*, 1865, 577), which boils at 144° . The compounds have the same boiling-point, and are both resolved by further oxidation into acetic and valerianic acids (Popoff, *Ann. Chem. Pharm.*, 145, 283). Erlenmeyer and Hell (*Ann. Chem. Pharm.*, clx, 257) have lately carefully examined the valerianic acids of different origins. They found that the acid obtained from the optically inactive amyl alcohol yields a crystallised barium salt, whilst that from the active alcohol forms an amorphous barium salt. I have not examined the optical properties of the alcohol which I employed for the preparation of the ethyl-amyl; but it was doubtless a mixture of active and inactive alcohols, as the two varieties always occur together, and thus probably the valerianic acid was also a mixture, the presence of the active acid preventing the crystallisation of the barium salt. The quantity of acid obtained was unfortunately too small for further examination.

The results of the investigation are, however, quite sufficient to prove that ethyl-amyl or dimethyl-butyl-methane is acted upon by chlorine in exactly the same manner as the normal paraffins.

I cannot conclude without taking this opportunity of expressing my thanks to Dr. Roscoe and Mr. Schorlemmer, for their kindness to me during the above research.