XXX.—CONTRIBUTIONS FROM THE LABORATORY OF THE LONDON INSTITUTION.

1. *The Oxidation-products of the Propione produced from Carbonic Oxide and Sodium-ethyl.*

By J. ALFRED WANKLYN.

THE progress of research has shown that the various ketones are characterised by their oxidation-products. I have, accordingly, oxidized the propione which is obtained by the action of carbonic oxide on sodium-ethyl.

The mode of preparing this propione has been already described.* Before employing the propione, I submitted it to a careful fractionation, so as to remove the liquid of high boiling point which accompanies it in its crude state. It was distilled ten times, and then heated in a current of dry carbonic acid to expel traces of ether.

After this preparation, I sealed some of it in a tube, together with excess of bichromate of potash and dilute sulphuric acid, and heated the whole in the water-bath for several hours. On opening the tube, no gas escaped, showing that carbonic acid is not among the oxidation-products. Moreover, the contents of the tube had the well-known smell of the acetic acid series.

After distilling and re-distilling, a distillate was obtained free from sulphates. This distillate was treated with carbonate of baryta, which dissolved very readily. An excess of the carbonate was then added and the liquid boiled and filtered.

The resulting solution of baryta-salt was evaporated to dryness in the water-bath, and the residue dried at 110° C.

Baryta determinations were made.

I. 0.3922 grm. of the barium-salt was ignited, when it evolved abundance of organic matter, and gave .2804 grm. of carbonate of baryta. *Percentage of barium* = 49.77.

II. 0.6266 grm. of the barium-salt was precipitated with dilute sulphuric acid, and the resulting sulphate of barium separated by filtration, washed, dried, and ignited. The sulphate of barium weighed 0.5295 grm. *Percentage of barium* = 49.74.

* Chem. Soc. J. [2], iv, 13 (1866).

The theoretical percentages of barium in the propionate and acetate are exhibited as follows:—

Propionate.			Acetate.		
C ₃	36	—	C ₂	24	—
H ₅	5	—	H ₃	3	—
Ba	68·7	48·48	Ba	68·7	53·75
O ₂	32	—	O ₂	32	—
<hr/>			<hr/>		
	141·7	100·00		127·7	100·00

Thus the percentage of barium is seen to be intermediate between that required by propionate, and that required by acetate, of barium.

Some of the barium-salt was carefully tested for formiates, which proved to be absent. It is, therefore, certain that the barium-salt consisted in part of acetate. A portion of the barium-salt was decomposed with an equivalent of dilute sulphuric acid, and the organic acid thus obtained was about half saturated with carbonate of soda and distilled. From the distillate a barium-salt was made.

0·2066 grm. of this barium-salt gave, on ignition with sulphuric acid, 0·1728 grm. of sulphate of barium. Percentage of barium = 49·24, which approximates sufficiently to the number required by propionate of barium. It will be apparent that had there been higher acids present, a treatment of this kind would have furnished a barium-salt having an entirely different composition.

The sodium-salt resulting from this partial saturation was distilled with dilute sulphuric acid. The distillate had all the characters of acetic acid, giving cacodyl when a salt of it was heated with arsenious acid, and acetic ether on treatment with alcohol and concentrated sulphuric acid.

There is, therefore, no doubt that propione is resolved quite simply into propionic and acetic acids, when it is oxidized with bichromate of potash and dilute sulphuric acid. This is, I believe, the first example of a ketone being resolved into acids of less carbon-condensation than itself, without at the same time giving rise to carbonic acid.

The generation of propionic and acetic acids from propione without production of carbonic acid is quite in accordance with theory.

It is not improbable that the first stage of the process consists in the formation of propionate of ethyl, *e. g.*,

and that there should be great difficulty in arresting the progress of the oxidation so as to exhibit the ether. Be this, however, as it may, the connection between the mode of origin of propione, and the production of its oxidation, deserves remark. Formed directly from carbonic oxide and ethyl, it admits of oxidation into acetic acid—the oxidation-derivative of the ethyl series—and propionic acid the oxidation-derivative of the propyl series. The oxidation of propione, an isomer of valeral ($\text{C}_8\text{H}_{10}\text{O}$), gives no acid higher in the scale than propionic acid.

2. *On the Oxidation of Ethylamine.*

By J. A. WANKLYN and ERNEST T. CHAPMAN.

WHEN ethylamine or sulphate of ethylamine is treated with bichromate of potash and sulphuric acid, little or no action takes place in the cold, even on long standing. On boiling, however, the ethylamine is attacked, though only slowly. As the solution becomes more concentrated, the reaction becomes brisker, and towards the end of the operation much gas is evolved. When the liquid has almost all distilled off, a reaction like that which takes place with ammonia and chromic acid occurs. Sulphate of ethylamine was boiled with bichromate of potash and dilute sulphuric acid. The vapours evolved passed first through a Liebig's condenser, and then into a receiver kept cool by ice and salt. The distillate was heated till a small quantity had distilled over. It smelt like aldehyde, and with it we obtained the ordinary reactions of that substance, *viz.*, formation of the silver mirror, and of the ammonia-compound.

The liquid which remained in the retort presented all the

characteristics of acetic acid. It was converted into a baryta-salt, and the per centage of barium determined.

·6306 grm. gave ·5738 Ba_2SO_4 or 53·5 per cent. Ba 53·7.

These numbers can leave no doubt that the substance in hand is acetic acid. A portion of the distillate which was supposed to contain aldehyde was heated in a sealed tube with a fresh portion of bichromate of potash and dilute sulphuric acid whereby it also was converted into acetic acid.

No ammonia could be detected in the mixture of chromate and sulphuric acid, even though examined before the violent final reaction. The method of examination adopted consisted in rendering a portion of the fluid from the retort, alkaline with potash, and then distilling into water; the solution so obtained was then neutralized with sulphuric acid and evaporated almost to dryness, and strong alcohol was added; this dissolves the sulphate of ethylamine, but not the sulphate of ammonia. This method of examination would not discover very small traces of ammonia, but would have detected any considerable quantity.

From the above it appears, therefore, that ethylamine yields by oxidation nitrogen, water, acetic acid and aldehyde.

3. *Action of Acids on Naphthylamine.* (Preliminary Notice.)

By ERNEST T. CHAPMAN.

IN a former paper, I mentioned several methods by which azodinaphthyldiamine may be produced.* These were;

First. Action of nascent hydrogen on dinitronaphthylin. (This method, however, I could not succeed in verifying.)

Second. Action of one equivalent of nitrous acid on two equivalents of naphthylamine. Both this and the preceding method were announced by Messrs. Perkin and Church.

Third. Action of nascent hydrogen on a mixture of nitro- and dinitronaphthalene.

Fourth. Action of zinc-ethyl on a similar mixture.

Fifth. Action of ammonia on a strongly acid solution containing naphthylamine and nitrous acid; it is to be remembered

* Chem. Soc. J. [2], iv, 135.

that potash cannot be substituted for ammonia in this preparation.

To these methods I may also add that a mixture of dry nitrite of potash and hydrochlorate of naphthylamine, if gently warmed, yields azodinaphthyl-diamine without difficulty, and only contaminated with chloride of potassium and the excess of nitrite employed.

I have now to announce an altogether new and very interesting method of obtaining this compound—one which, I think, is calculated to throw a new light on the atomic constitution of naphthylamine.

I observed, when previously working on these compounds, that naphthylamine is soluble in concentrated sulphuric acid, but that, on diluting this solution, I could not succeed in making it crystallise. As it is a well known fact that naphthylamine-salts frequently assume a colloid form, I did not investigate the causes of this phenomenon. Some observations, which I subsequently made, led me to examine this solution more carefully. I dissolved naphthylamine in cold concentrated sulphuric acid, and allowed it to stand over night. On examining it next morning, I found that it was perfectly colourless, and on diluting it with water and adding potash, a red precipitate was produced, instead of the white one, which might have been expected. This red precipitate, on the addition of acids, assumed a violet colour and was in short, azodinaphthyl-diamine. I naturally suspected oxides of nitrogen to be present in the sulphuric acid employed. This, however, was not the case. I then warmed some of the original solution. It became brilliantly green, the upper surface of the fluid being violet. On being poured into water, it did not immediately mix with it, and when it did mix, it turned violet. The violet colouring matter gradually separated out and was filtered off. It presented all the characters of a salt of azodinaphthyl-diamine. These characters are, insolubility in water, solubility in alcohol, the solution being a most magnificent violet, which is changed to an orange on the addition of an alkali; the original colour is re-obtained by the addition of an acid: if the acid be added drop by drop, the colour passes through various shades of red, crimson, and lilac before it re-assumes the original violet colour. It dissolves in concentrated sulphuric acid with a very beautiful blue colour. From this solution it is precipitated unaltered on the addition of water.

As many persons might consider the reactions of azodinaphthyl-diamine insufficient to establish its identity with the substance described in this paper, I have, with great labour, succeeded in obtaining a well crystallised sample, and determined the percentage of nitrogen it contained. It yielded the following numbers:—

·6405 of the base gave 77·5 c. c. N. (moist). Bar 755. Temp. 14° C.

∴ 75·4 c. c. at 760 bar. and 0° C.

∴ % of N. in substance 14·75.

Theory 14·14.

The preceding observations naturally led to a general examination of the action of acids on naphthylamine. The acids employed were the following:—Nordhausen sulphuric acid, and common sulphuric acid, phosphoric acid (obtained from the residue in the preparation of iodide of ethyl, and, therefore, free from all suspicion of oxides of nitrogen), oxalic, acetic, tartaric, citric, nitric, hydriodic, and hydrochloric acids. All these acids, with the exception of hydrochloric acid, when boiled with water and naphthylamine, produce colourless or but slightly coloured compounds, which, by the action of potash, yield azodinaphthyl-diamine. The nitric acid must, of course, be used dilute. The other acids appear to act best when concentrated, and indeed the largest yield is obtained by fusing together naphthylamine and oxalic acid. The resulting compound must be dissolved in boiling water, and precipitated with potash, carbonate of potash, or in some cases ammonia*. Curiously enough, I could not make hydrochloric acid produce this conversion of naphthylamine into azodinaphthyl-diamine. On a consideration of this reaction, it is evident that at least three equivalents of naphthylamine must be concerned in the formation of one of azodinaphthyl-diamine, and that there must also be secondary products formed. Of course the simplest view of the case is that three equivalents of naphthylamine coalesce, and that $C_{10}H_{12}$ is in some manner eliminated from them by the action of the acid. I have not yet succeeded in isolating the secondary product.

* Ammonia will answer in the case of sulphuric acid, but gives a colourless solution with the oxalic acid. I have not tried its action with any of the other acids.

Aniline (crude) apparently behaves in a similar manner, though I have not examined its action with any acid excepting sulphuric acid. If naphthylamine be boiled with dilute sulphuric acid, the resulting colourless solution need not be treated with an alkali or an alkaline carbonate; acetate or oxalate of potash produces the same effect, though of course the acetate or oxalate of the base is obtained instead of the base itself.

Sometimes the colourless solution obtained by boiling the naphthylamine with excess of acid yields only traces of the base on the addition of an alkali; nevertheless, the base itself may easily be obtained from such a solution by re-acidifying and re-precipitating.

When naphthylamine is heated with excess of hydrochloric acid, it yields, as usual, a colourless solution, which yields a red base by the addition of an alkali. This base, however, is not turned violet by the addition of an acid, but again becomes colourless. The only body, known to me, derived from naphthylamine having this peculiarity is ninaphthylamine. I have not examined the body, and cannot, therefore, do more than suggest the possibility of this red base being ninaphthylamine. I have worked with ninaphthylamine, and the substances present precisely similar appearances.

It has often been remarked, on attempting to recrystallise salts of naphthylamine, that they are apt to lose their power of crystallisation, and to become gummy. It is also well known that solutions of these salts cannot be kept without undergoing a similar change. On examining the mother-liquor from which the sulphate had been crystallised, I found that it yielded azodinaphthyldiamine by the action of alkalies.

Every one who has ever worked with naphthylamine must have observed that filter-papers, cloths, and, in fact, everything which comes much in contact with the solutions, assumes a reddish or violet colour, and I have observed that such papers may be turned orange by the action of an alkali, and regain their violet colour when acted upon by acids. It would appear, therefore, that this coloration is due to azodinaphthyldiamine.

4. *Production of Acetic and Propionic Acids from Amylic Alcohol.*

By ERNEST T. CHAPMAN.

THE starting point of the following investigation was nitrite of amyl. This substance was prepared from the alcohol by the action of nitrous acid in the usual manner. It was found to boil constantly at 98°C ., with the barometer at 750 mm.

The nitrite having been very carefully dried, was treated with anhydrous phosphoric acid. A violent reaction at once took place. The mixture became very hot—so hot that in one instance it took fire. The reaction may, however, be rendered quite manageable by cooling the vessel with water, and adding the nitrite little by little. Care should be taken *not* to add excess of nitrite. The reaction is not accompanied by disengagement of gas. The product is a brown solid mass.

A portion of it was heated with strong solution of potash. The distillate had a mouldy, ammoniacal smell, and strong alkaline reaction. It was rendered slightly acid with hydrochloric acid, evaporated almost to dryness, and bichloride of platinum was added in excess. A precipitate was soon formed. It was washed, dried, and the percentage of platinum determined. It corresponded with ammonio-bichloride of platinum.

The filtrate was then rendered slightly alkaline with potash when the mouldy smell was again produced; it has considerable resemblance to patchouli. On rendering the fluid strongly alkaline and heating, the smell of ammonia was again perceived. The mixture was then distilled, the distillate mixed with excess of strong potash, and heated in a sealed tube for about an hour at 120°C .

When the tube was opened, gas escaped, and there was a strong smell of ammonia, but the mouldy smell had disappeared. The contents of the tube were rendered acid with sulphuric acid, transferred to a small retort, and distilled. The distillate was free from sulphuric acid, but had a strongly acid reaction. It tasted and smelt like acetic acid. Another portion of the original substance was heated with caustic potash in such a manner that the fluid distilling off flowed back again on to the potash. Ammonia

was evolved, and the contents of the retort when distilled with sulphuric acid yielded a distillate free from sulphuric acid, but possessing a strongly acid reaction. It was neutralised with carbonate of baryta, boiled, and filtered. A measured volume of this solution was then evaporated to dryness, and the percentage of barium determined.

·2851 grm. salt gave ·2484 grm. Ba_2SO_4 ,
or 50·9 per cent.

This number is intermediate between 48·34, the percentage of propionate, and 53·72, the percentage of acetate.

Enough sulphuric acid was added to neutralise one-third of the baryta in another measured volume of this liquid, and the liquid was distilled. The distillate was then neutralised with carbonate of baryta, evaporated to dryness, and the percentage of barium determined.

·4675 grm. of the salt gave ·3848 Ba_2SO_4 .
∴ 48·45 % Ba. Theory 48·34.

As will be seen from the results, the numbers correspond with those required by the propionate. To the liquid in the retort as much more sulphuric acid was added, and the acid thereby liberated boiled off. As this liquid was sure to contain a mixture of the two acids, it was not further examined.

More sulphuric acid was then added, the distillate thus obtained was neutralised with carbonate of baryta, boiled, and filtered, the liquid was evaporated to dryness, and the percentage of barium determined.

·5482 grm. salt gave ·5000 grm.
∴ 53·68 % Ba. Theory 53·72.

This number corresponds with that required by acetate of baryta.

I have not been able to obtain the compound which has the mouldy smell free from ammonia, nor do I see how I could do so, as, when it is liberated from its compounds with acids by the action of potash, it always breaks up into ammonia and acids. A portion of the original substance was heated gently with strong potash-solution, and the liquid rendered acid by hydrochloric

acid. Under these circumstances, an acid with a most remarkable odour separates out, but I have not succeeded in obtaining any of its salts. When I attempted to recrystallise any of these compounds they underwent decomposition, and as I had not much of the substance, I abandoned the attempt. The nature of the above-mentioned reactions seems to be as follows:—

First. $C_5H_{11}NO_2$, by the action of P_2O_5 , is deprived of 2 eqs. of water, and is converted into C_5H_7N .

C_5H_7N may be regarded as the cyanide of an alcohol-radical of the allyl series (C_4H_7Cy). This, when acted upon by potash, should give ammonia and an acid isomeric or identical with angelic acid. Now, angelic acid, as is well known, splits up when heated with potash, yielding acetic and propionic acids:

The most remarkable thing about this reaction is the ease with which it takes place, even at comparatively very moderate temperatures.

The question naturally suggests itself what would be the action of anhydrous phosphoric acid on other members of the same class of ethers. What, for instance, would happen if the nitrite of ethyl were treated in the same way? Should we obtain 2 eqs. of formic acid as the last product? And what could we obtain from nitrite of methyl?

Phosphoric acid attacks nitrates as well as nitrites, though not so easily, and this may prove to be a method of obtaining compounds of the same class as picoline.

There is one aspect of the subject which deserves attention. In the reactions above described, we have seen that ordinary amyl alcohol splits up into the groups C_3 and C_2 . Why does it not split up into the groups C_4 and C ? Possibly ordinary amyl alcohol is not strictly a primary alcohol.

5. *On some Decompositions of Nitrite of Amyl.*

By ERNEST T. CHAPMAN.

1st. *Action of Oxidizing Agents :—*

Nitrite of amyl was treated with bichromate of potash and sulphuric acid. The operation was conducted in a retort with a condenser so arranged that the condensed vapours ran back into the retort. Bichromate of potash and dilute sulphuric acid were introduced into the retort and raised to the boiling point. The nitrite was then added drop by drop from a stop-cock dropping funnel. The reaction is very brisk, but no permanent gas is evolved. As soon as the reaction was finished, about a third of the contents of the retort were distilled over. The distillate consisted of two layers, and had a smell resembling that of pine apples; it was agitated with carbonate of soda. Brisk effervescence ensued and a considerable portion of the oily layer disappeared, the remainder was decanted, dried over chloride of calcium (of which it dissolves a considerable quantity,) distilled off and fractionally distilled. It began to boil at 130° , but only a few drops passed over until the temperature had reached 185° , between which and 187° the whole of the liquid distilled over. A portion of the distillate was digested with caustic potash in aqueous solution. The product of this operation was put into a retort and about a third distilled over. The distillate consisted of two layers. It was saturated with sulphate of soda, which greatly increased the amount of the oily layer; this latter was then decanted, dried, and distilled. It presented all the characteristics of ordinary amylic alcohol, boiling point 132° . The liquid remaining in the retort was then rendered strongly acid with sulphuric acid, and a portion distilled over. This distillate also separated into two layers and presented the smell and characters of valerianic acid. A portion of the oily layer was dried and distilled; it boiled at 173° . The remainder of the distillate was boiled with excess of carbonate of baryta, filtered, evaporated to dryness, and the percentage of barium determined: it yielded the following numbers :—

Salt taken .4466
 $\therefore$ Ba % 40.32

Ba₂SO₄ found .3062
 Theory 40.42

The aqueous portion of the original distillate was boiled, with a view of expelling any of the oily matters that might have remained in solution. To a portion of it, iodide of potassium, acetic acid, and starch-paste were added: no blue coloration was produced, whence the absence of nitrites may be inferred. Another portion of this liquid was then tested for nitrates with proto-salt of iron and sulphuric acid; nitric acid was present in abundance. The liquid was now saturated with sulphate of soda, and dilute sulphuric acid added; an oily layer at once rose to the surface. It was decanted, dried, and distilled, it also boiled at 173° , and smelt like valerianic acid. It was converted into a baryta-salt and the percentage of barium determined. It gave the following numbers:—

Salt taken	·3938	Ba_2SO_4 found	·2700
∴ Ba %	40·32	Theory	40·42

From the above it appears that nitrite of amyl is converted by the oxidizing action of chromic acid into nitric acid, valerianic acid, and valerianate of amyl.

2nd. *Action of Sulphuric acid on Nitrite of Amyl.*

Concentrated sulphuric acid attacks nitrite of amyl with great energy, red fumes are evolved in abundance, and occasionally the liquid catches fire. The product is a black, foul-smelling liquid. As charring evidently takes place, it was not further examined. I then made some experiments to determine how dilute an acid could be employed to effect this decomposition, and, after many trials, came to the conclusion that the best acid to employ was a mixture of two volumes of water and one of concentrated sulphuric acid. This liquid has little or no action on the nitrite in the cold, but at a few degrees above 100°C . it attacks it pretty readily. The apparatus employed in this experiment was similar to that already described, with the exception that arrangements were made to collect and examine the gas evolved.

Great care is required in this experiment, as, if the temperature rises too high, charring occurs, and of course the result is complicated by secondary products; if the temperature is not sufficiently high, the decomposition proceeds irregularly, and the evolution of gas takes place in bursts. The nitrite of amyl was added drop by drop, and the temperature so regulated as to keep up a gentle and continuous evolution of gas.

Examination of the gas :—The gas when collected over mercury

or water is perfectly colourless ; if collected over mercury, or if examined immediately after being collected over water, it appears to be inflammable, this, however, is due to vapours suspended in the gas ; for on agitation with water, this property disappears. If a stream of the gas be directed into a damp flask, the flask is immediately filled with red fumes, and a white crystalline substance is deposited. On dissolving this in water, and adding chloride of barium and hydrochloric acid, an abundant precipitate is at once obtained. The gas is completely soluble in solution of protochloride of iron. It contains no carbonic acid, as was conclusively proved by the following experiment. A Liebig's potash apparatus was charged with a mixture of bichromate of potash, chloride of barium, and dilute hydrochloric acid. When the gas was passed slowly through this and then into lime water, not the slightest turbidity was produced, though sulphate of baryta was precipitated in the potash bulbs ; it appears, therefore, that the gas is a mixture of sulphurous acid and nitric oxide ; and further that no other gas is present.

Examination of the liquid products. As soon as the smell of nitrite of amyl had disappeared, water was added and about one-third of the contents of the retort was distilled off and treated precisely in the same manner as that described in the former section (action of oxidizing agents). It yielded, first, a neutral oily liquid boiling at the same temperature as the valerianate of amyl mentioned in the previous experiment (186°C.), and having the same odour. By treatment with potash it yielded a liquid having the characteristics of amylic alcohol, and also an acid having the smell and saturating capacity of valerianic acid, as shown by the following determination of the percentage of barium in its baryta salt :—

Salt taken ·3088	BaSO ₄ found ·2124
∴ Ba % 40·44	Theory 40·42

2nd. A very small quantity of valerianic acid was dissolved out of the original distillate by carbonate of soda. Converted into a baryta salt it yielded the following numbers :—

Salt taken ·2916	BaSO ₄ found ·2004
∴ Ba % 40·39	

I find, therefore, that nitrite of amyl and sulphuric acid react upon each other, producing sulphurous acid, water, and valeria-

nate of amyl. The trace of valerianic acid formed is doubtless due to a secondary reaction. The following equation would show the change :—

3rd. *Action of Hydriodic acid on Nitrite of Amyl.*

Concentrated hydriodic acid acts upon nitrite of amyl in the cold, very little rise of temperature taking place, although iodine is liberated abundantly.

Concentrated hydriodic acid and phosphorus were introduced into the apparatus already described, gently warmed, and nitrite of amyl added drop by drop. A colourless gas is evolved in abundance, which produces dense red fumes on coming in contact with the air; it is completely soluble in protochloride of iron, and is, in fact, nitric oxide.

On distilling the contents of the retort, a heavy oily liquid passes over. It was washed with dilute solution of carbonate of soda, dried over chloride of calcium, and distilled. It boiled constantly at 146°C . A weighed quantity of it was digested with alcoholic potash, and the amount of iodine determined; .3624 of the substance gave .4276 of iodide of silver.

$$\therefore 63.76 \% \text{ I} \qquad \text{theory} \qquad 64.13 \% \text{ I}$$

These numbers can leave no doubt that the substance in hand is iodide of amyl.

Permanganate of potash also oxidizes nitrite of amyl. I have not fully investigated the products, but they appear to be the same as those obtained by the action of chromic acid.