

XXXII.—*Action of Phosphoric Anhydride on Fatty Acids.* Part I.

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AT a moderately high temperature, some fatty acids are decomposed by phosphoric anhydride with evolution of carbonic anhydride and formation of a ketone. This reaction may be represented by the equation—



Normal heptylic and stearic acids are the only compounds which have yet been systematically investigated in this direction, and in both cases a considerable quantity of the ketone is formed.

The only methods of any general application at present employed for the preparation of fatty ketones of the formula $R_2\text{CO}$ are, as is well known, (1) by the distillation of the calcium or barium salts of the fatty acids, and (2) by the action of acid chlorides on the zinc compounds of the alcohol radicles.

The first of these methods cannot be considered satisfactory as regards either the quantity or the purity of the ketone obtained. By the distillation of calcium acetate, for example, Fittig found that not only acetone, but also the homologous ketones of the composition $\text{C}_4\text{H}_8\text{O}$ and $\text{C}_5\text{H}_{10}\text{O}$ were formed, whilst calcium butyrate gives, in addition to butyrone, the homologues $\text{C}_5\text{H}_{10}\text{O}$, $\text{C}_6\text{H}_{12}\text{O}$, $\text{C}_8\text{H}_{16}\text{O}$, and $\text{C}_{11}\text{H}_{22}\text{O}$ (Limpricht, *Annalen*, **108**, 183; and Friedel, *ibid.*, 122); in both cases, therefore, the purification of the principal product would be a tedious and difficult process.

The other general method for the preparation of ketones is also an unsatisfactory one; it is troublesome to carry out and the materials employed are both expensive and difficult to prepare.

The experiments described below seem to show that ketones, or at any rate the higher members of the series, can be easily prepared by treating the fatty acids with phosphoric anhydride under suitable conditions. In the case of heptylic acid, two experiments, carried out under different conditions, gave 33 and 25 per cent. respectively of the theoretical quantity of pure dihexyl ketone, $(\text{C}_6\text{H}_{13})_2\text{CO}$, whilst with stearic acid the yield of pure stearone, $(\text{C}_{17}\text{H}_{35})_2\text{CO}$, is at least 40—42 per cent. of the theoretical; further experiments have yet to be made, in order to ascertain the conditions which give the best yield of the desired product.

In both reactions considerable quantities of other products are formed, but these are of such a nature that no difficulty whatever is

experienced in isolating the ketones and obtaining them in a pure condition.

Experiments have already been commenced on the action of phosphoric anhydride on other acids, both of the fatty and aromatic series; their behaviour with zinc chloride and other dehydrating agents is also being investigated.

Preparation of Dihexyl Ketone, (C₆H₁₃)₂CO.

Several experiments have been made with normal heptylic acid at temperatures varying from 140° to 220°, and with different quantities of phosphoric anhydride, in order to ascertain the most suitable conditions for the preparation of dihexyl ketone; the best results were obtained in the following manner:—10 grams of anhydrous heptylic acid are heated at 180° in a small flask placed in a metal- or oil-bath, and 6·5 grams of phosphoric anhydride is quickly added in three portions, the mixture being stirred well during the process; at first a considerable quantity of carbonic anhydride is evolved, and the temperature rises 10° or 15°, but the reaction is quickly at an end, the whole operation requiring only about three minutes. The flask is then taken out of the bath, allowed to cool, and the dark-brown mass gradually stirred up with water; the fact that there is little or no development of heat shows that the whole of the phosphoric anhydride has been changed, even when, as in this experiment, a quantity considerably in excess of the theoretical is employed.

The solution is now rendered strongly alkaline with potash or soda, and the contents of the flask transferred to a larger flask and distilled with steam; the ketone collects in the receiver in the form of a yellowish oil which, on cooling, solidifies to almost colourless, waxy plates. The crystalline substance is separated by filtration, allowed to dry in the air for a short time, and then spread on a porous plate to free it from traces of oily impurities.

It is thus obtained in an almost pure condition in colourless crystals melting at 28—30°.

1·4 grams of dihexyl ketone are obtained in this way from 10 grams of heptylic acid, but a considerable quantity of unchanged acid remains as sodium or potassium salt in the alkaline residues from which the ketone has been distilled. In order to isolate this acid, the alkaline solution is strongly acidified with dilute sulphuric acid and again distilled with steam; the aqueous distillate is extracted twice with ether, the ethereal solution dried over calcium chloride, and the ether evaporated. The heptylic acid (4 grams) which is thus obtained is almost pure, as shown by its behaviour on distillation, and can be directly employed for another operation.

Since, then, 6 grams of heptylic acid give 1.4 grams of dihexyl ketone, the yield is 33 per cent. of the theoretical.

In another experiment, the operation was carried out as described above, except that the heptylic acid (6 grams) was heated almost to boiling, then 3.5 grams of phosphoric anhydride added in small portions at a time, and the mixture heated again for about three minutes; the whole process required about six minutes. The ketone obtained, isolated as described above, weighed 0.95 gram, and 1 gram of unchanged acid was obtained from the alkaline residues. The yield in this experiment was, therefore, 25 per cent. of the theoretical.

The crude ketone can be easily obtained in a perfectly pure condition by dissolving it in methyl alcohol and reprecipitating with cold water; it separates from the solution in transparent, waxy plates melting at 30.5°.

An analysis of a portion which had been dried on a porous plate and then kept over sulphuric acid for 24 hours gave the following result:—

0.1608 gram of substance gave 0.4637 gram of CO₂ and 0.1886 gram of H₂O.

	Calculated for C ₁₃ H ₂₆ O.	Found.
C.....	78.78 per cent.	78.65 per cent.
H.....	13.13 „	13.03 „
O.....	8.09 „	8.32 „

Dihexyl ketone (œnanthone) has been previously prepared by Uslar and Seekamp (*Annalen*, **108**, 179) by the distillation of calcium œnanthylate. In their paper, the authors state that various oily products are also formed in the reaction, and that the dihexyl ketone can be obtained in a pure condition (melting at 30°) only by repeated fractional distillation; the yield of ketone is not given, and its preparation in this way is evidently a tedious operation. Dihexyl ketone (melting at 30.5°) was also obtained in small quantities by Fittig (*Annalen*, **117**, 80) in a somewhat similar manner, together with large quantities of other products; the yield is not given, and the properties of the ketone are not described.

The dihexyl ketone obtained by the action of phosphoric anhydride on heptylic acid, after being once crystallised from dilute alcohol, melted at 30.5°, in agreement with Uslar and Seekamp's and Fittig's observations. It is very readily soluble in alcohol, ether, chloroform, light petroleum, and all organic solvents, but seemingly insoluble in water. If the aqueous distillate, referred to above, from which the ketone has been separated by filtration, is extracted with ether, and the dried ethereal solution evaporated, there remains only a trace of a

yellowish oil which does not solidify on cooling. Dihexyl ketone is not very readily volatile with steam, but it distils without decomposition under the ordinary pressure. It seems to be only slowly oxidised by nitric acid or by an alkaline solution of potassium permanganate. That the compound obtained from heptylic acid, as described above, is in reality dihexyl ketone is proved, not only by its melting point and the results of analysis, but also by the formation of the oxime and the hydrazone, and by its behaviour on reduction.

Considerable quantities of bye-products are formed in the preparation of dihexyl ketone, and, after distilling the ketone (or acid) with steam, there remains in the flask a thick, almost black oil which can be easily isolated by extracting with ether. This substance has as yet only been superficially examined; it distils at a high temperature under greatly reduced pressure, yielding a thick, yellow liquid which has an odour recalling that of heptylic acid.

Oxime of Dihexyl Ketone, (C₆H₁₃)₂C:N·OH.

Dihexyl ketone oxime can be easily prepared by treating the ketone with hydroxylamine by Auwers' method. 1 gram of the pure ketone is dissolved in methyl alcohol, a dilute alcoholic solution of hydroxylamine hydrochloride (0·6 gram) and potash (2 grams) added, and the mixture heated to about 60°. After keeping for about 24 hours at the ordinary temperature, the alcohol is evaporated on the water-bath, the residue mixed with water and the solution acidified with dilute hydrochloric acid. The precipitated oil is then extracted with ether, the ethereal solution dried over calcium chloride and evaporated. The yellow oil obtained in this way was kept over sulphuric acid under reduced pressure for some days, and then analysed.

The following is the result:—

0·2005 gram of substance gave 12·3 c.c. of nitrogen, measured at 740 mm. and 16°.

	Calculated for C ₁₃ H ₂₇ NO.	Found.
N.....	6·6 per cent.	6·95 per cent.

Dihexyl ketone oxime is a yellowish oil which shows no signs of crystallising even when cooled below 0°; it is very sparingly soluble both in acids and alkalis, and seemingly insoluble in water, but miscible with alcohol, ether, &c., in all proportions.

Hydrazone of Dihexyl Ketone (C₆H₁₃)₂C:N·NHPh.

This compound was obtained by heating the pure ketone at 100° for about two hours with excess of phenylhydrazine and a little

alcohol. The solution was then treated with water, the separated oil extracted with ether, and the ethereal solution washed well, first with dilute hydrochloric acid and then with water. On evaporating the dried ethereal solution, the hydrazone remains as a thick, reddish-yellow oil; it was kept for 48 hours over sulphuric acid under reduced pressure, and then analysed with the following result:—

0.2287 gram of substance gave 20 c.c. of nitrogen, measured at 740 mm. and 12°.

	Calculated for $C_{19}H_{32}N_2$.	Found.
N.....	10.0 per cent.	10.1 per cent.

Dihexyl ketone hydrazone is a moderately thick, reddish-yellow oil: it is insoluble in water and potash, but readily soluble in alcohol, ether, and other organic solvents. It dissolves sparingly in concentrated hydrochloric acid yielding a pink solution, but on keeping for a short time or heating gently, the hydrazone decomposes with evolution of gas. When heated in small quantities under the ordinary pressure, it decomposes with slight explosion, but without noise.

Dihexyl Carbinol, $(C_6H_{13})_2CH \cdot OH$.

Dihexyl carbinol can be easily prepared by reducing the ketone in the following manner:—The pure compound is dissolved in a considerable quantity of pure ether and the ethereal solution placed in a large flask or bottle provided with a reflux condenser and containing 100—200 c.c. of moderately concentrated caustic soda; sodium is then added, in small portions at a time, the total quantity employed being greatly in excess of that theoretically required for complete reduction. During the process, the ethereal solution gradually becomes turbid, owing to the separation of a colourless solid compound—probably the sodium-derivative of the alcohol—but on agitating with the aqueous solution, this substance disappears and the solution becomes clear again. The ethereal solution is then separated, the residual alkali extracted twice with ether, the combined ethereal solutions dried over potassium carbonate, and the ether evaporated.

Dihexyl carbinol is thus obtained in the form of a thick, yellowish oil which soon solidifies completely to a mass of crystals. It is best obtained in a pure condition by dissolving it in cold methyl alcohol and reprecipitating with water; if the addition of water causes the separation of an oil, it is advisable to cool the alcoholic solution in

a freezing mixture before diluting, otherwise crystallisation takes place only after long standing. The colourless crystals are then separated by filtration and dried first on a porous plate and then over sulphuric acid.

An analysis of the crystalline alcohol gave the following result:—

0.1517 gram of substance gave 0.4324 gram of CO_2 and 0.1924 gram of H_2O .

	Calculated for $\text{C}_{13}\text{H}_{28}\text{O}$.	Found.
C	78.0 per cent.	77.74 per cent.
H	14.0 „	14.09 „
O	8.0 „	8.17 „

Dihexyl carbinol separates from dilute alcohol in colourless, transparent plates melting at $41\text{--}42^\circ$; it has a peculiar sweet odour, and is very readily soluble in light petroleum, benzene, chloroform, alcohol, and other organic solvents, but insoluble in water. When heated in small quantities under the ordinary pressure, it distils without decomposition, and the distillate quickly solidifies on cooling. When treated with cold concentrated hydrobromic acid, the crystals melt to a yellowish oil, but do not dissolve in the acid; on diluting with water, this oil solidifies to colourless plates which melt at $38\text{--}39^\circ$. This compound is doubtless the bromide, $(\text{C}_6\text{H}_{13})_2\text{CHBr}$, as it contains considerable quantities of bromine.

Preparation of Stearone $(\text{C}_{17}\text{H}_{35})_2\text{CO}$.

The stearic acid employed in these experiments was obtained by repeatedly recrystallising the crude commercial acid from strong alcohol; that the acid was pure is shown by its melting point ($68\text{--}69^\circ$) and by the following analysis:—

0.1490 gram of substance gave 0.4150 gram of CO_2 and 0.1692 gram of H_2O .

	Calculated for $\text{C}_{18}\text{H}_{36}\text{O}_2$.	Found.
C	76.05 per cent.	75.96 per cent.
H	12.67 „	12.61 „
O	11.28 „	11.43 „

It is perhaps a fact worthy of remark that stearic acid which has been crystallised from alcohol retains some of the solvent even after long exposure to the air on a porous plate, and its melting point is thereby lowered considerably.

For the preparation of stearone, the following method was em-

ployed:—9·5 grams of pure stearic acid are placed in a small beaker and heated at 210° in a metal- or oil-bath; 5 grams of phosphoric anhydride are then added in small portions at a time, the mixture being stirred well during the process. At first, considerable effervescence takes place, owing to the liberation of carbonic anhydride, as can be easily proved in the usual manner; towards the end of the operation, no further evolution of gas occurs. The dark-brown mass is allowed to cool, and then gradually stirred up with water. A considerable quantity of phosphoric anhydride remains unchanged, as is shown by the development of heat on adding water, and it is probable that a better yield of ketone would be obtained by using less anhydride than the quantity given above; if, on the other hand, too small a quantity of phosphoric anhydride were employed, some of the stearic acid would remain unchanged and the purification of the ketone would be less simple. After adding excess of soda or potash, the mixture is warmed gently, with frequent stirring, for about 15 minutes, then allowed to cool, diluted with water, and the alkaline solution of phosphate separated by filtration, or more quickly, by decantation; it has been found advisable not to boil the alkaline liquid, as, if this be done, a sort of emulsion is formed and the insoluble products cannot easily be separated.

The insoluble wax-like mass is washed with water, transferred to a flask, and repeatedly extracted with strong alcohol. This process is greatly facilitated if some filter-paper is placed in the flask; the insoluble oily products are then absorbed by the paper, and the alcoholic extract remains quite clear, so that it is unnecessary to filter the solution. On cooling, the alcoholic extracts deposit the stearone completely in the form of a yellowish powder; it is separated by filtration and dried on a porous plate.

The yield of crude stearone was 3·5 grams from 9·5 grams of stearic acid, or 41 per cent. of the theoretical quantity. Only two experiments with stearic acid have as yet been made, so that it is probable that the process can be considerably improved.

The crude product is almost pure, and melts at about 84 — 85° ; by crystallising it twice or three times from alcohol, it is obtained in a perfectly pure condition, and then melts at 88° .

Analyses of two different samples of the pure compound, dried at 100° , gave the following results:—

- I. 0·1323 gram of substance gave 0·4026 gram of CO_2 and 0·1643 gram of H_2O .
- II. 0·1420 gram of substance gave 0·4316 gram of CO_2 and 0·1771 gram of H_2O .

	Calculated for $C_{35}H_{70}O$.	Found.	
		I.	II.
C	83·00 p. c.	82·99	82·88 p. c.
H	13·83 „	13·83	13·85 „
O	3·17 „	3·18	3·27 „

Stearone has been previously prepared by Heintz (*Jahresb.*, 1855, 515—516) by the distillation of stearic acid alone or with lime; also by Krafft (*Ber.*, 15, 1715), by the distillation of calcium stearate under reduced pressure. I have not been able to refer to Heintz's paper, but Krafft, who improved the original process, states that the yield does not amount to half the theoretical.

By the method described above, stearone can be easily obtained in a pure condition in the course of a few hours with comparatively little trouble, and the yield, as already mentioned, is at least 40 per cent. of the theoretical. It is necessary, however, that the pure acid should be employed; in some experiments with a sample of the commercial acid, melting at about 62°, the ketone obtained melted at 75—76°, even after being repeatedly recrystallised from alcohol, probably owing to the presence of palmitone and other homologues.

It is stated in "Beilstein" (1886, p. 421) that when stearic acid is heated with phosphoric anhydride, it yields a compound of the composition $C_{18}H_{34}O$ which melts at 54—60°, and is insoluble in alkalis. I have not been able to detect the formation of any substance of this nature; it is evidently not present as impurity in the stearone, because, if it were, the analyses would indicate the fact, the two compounds $C_{35}H_{70}O$ and $C_{18}H_{34}O$ differing considerably in composition, especially as regards the percentage of hydrogen which they contain. As is the case with heptylic acid, a considerable quantity of bye-products are formed in the action of phosphoric anhydride on stearic acid; after extracting the product with alcohol until ketone ceases to be deposited on cooling, there remains a brown, waxy substance which is practically insoluble in alcohol, but readily soluble in benzene or light petroleum. This product has not yet been examined, but it seems hardly probable that it should be a compound of the composition $C_{18}H_{34}O$.

Stearone Oxime, $(C_{17}H_{33})_2C:N\cdot OH$.

For the preparation of this compound 0·7 gram of the stearone, obtained as described above, was dissolved in hot alcohol, 0·3 gram of hydroxylamine hydrochloride and 0·5 gram of potash, dissolved in a little dilute alcohol, added to the solution, and the mixture boiled in a flask, provided with a reflux condenser, for about two hours. The

solution, on cooling, deposited a colourless powder which was separated by filtration, washed well with very dilute hydrochloric acid, then with water, and dried on a porous plate.

This substance is stearone oxime, as is shown by the following analysis :—

0.2514 gram of substance gave 6.6 c.c. of nitrogen, measured at 755 mm. and 14°.

	Calculated for $C_{35}H_{71}NO.$	Found.
N.....	2.68 per cent.	3.07 per cent.

It separates from hot alcohol as a colourless, seemingly amorphous powder and melts at 63°; it is moderately easily soluble in boiling benzene and hot alcohol, but insoluble in alkalis, acids, and water.

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