LIV.—*Paraheptotoluene and its Derivatives.*

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In a recent paper (*Trans.*, 1894, **65**, 480), it was shown by one of us that phenylpropionic chloride may be directly converted into hydrindone by the action of aluminium chloride, and that under suitable conditions this process affords an excellent method for the preparation of this ketone. As this was the first case in which an action of the kind had been studied and, as it appeared desirable to extend its application, experiments with other acid chlorides were commenced, and in the first place the action of aluminium chloride on heptonic chloride was investigated. This particular compound was chosen, not so much because it seemed the one most likely to undergo the desired change, but because, if it had done so, and had led to the formation of methylketohexamethylene, $\text{CH}_3\cdot\text{CH}<\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CO}\cdot\text{CH}_2 \end{smallmatrix}>\text{CH}_2$, or of ethylketopentamethylene, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}<\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CO}\cdot\text{CH}_2 \end{smallmatrix}>$, as seemed possible, the results would have been of considerable interest.

The first experiments were not successful ; for although on warming heptioic chloride with aluminium chloride a very vigorous action occurred, and dense fumes of hydrogen chloride were evolved, most of the acid chloride was ultimately recovered in the form of heptioic acid and only a very small quantity of a neutral oil was produced ; this oil, moreover, was evidently of a complex character and no definite compound was isolated from it. As, however, the previous investigation of this reaction in the case of phenylpropionic chloride had shown that so much depended on the conditions under which the substances are brought together, these unsatisfactory results were not taken as conclusive, and one of us (Russell) undertook a series of experiments to ascertain the effect of a change of temperature and of using different diluents ; it was thus found that when "light petroleum" boiling at 100—110° was employed as a diluent a considerable proportion of the heptioic chloride was converted into a neutral oil, from which a crystalline compound was ultimately isolated by fractional distillation. This product was found to be a ketone of the composition $C_{14}H_{20}O$, and at first we thought that it had been formed from the heptioic chloride in accordance with the equation $2C_6H_{13} \cdot COCl = C_{14}H_{20}O + 2HCl + H_2O + H_2$.

Further investigation, however, proved it to be a paraheptotoluene of the constitution $CH_3 \cdot C_6H_4 \cdot CO \cdot [CH_2]_5 \cdot CH_3$, and it was finally ascertained that its formation under the conditions mentioned above was due to the fact that the "light petroleum" used as a diluent accidentally contained toluene.

In this paper, therefore, we simply give an account of various compounds, which were prepared and analysed in the course of these experiments, and which have not hitherto been described ; the original object of this investigation, namely the conversion of heptioic chloride into a ketone by the elimination of hydrogen chloride, has not been attained, and as it has recently come to our knowledge that Combes has already succeeded in preparing triethylphloroglucinol from butyric chloride under similar conditions (*Compt. rend.*, 1894, **118**, 1336), further experiments will not be made.

Having had at our disposal a considerable quantity of paraheptotoluene, we have investigated its behaviour with phosphoric anhydride and found that at its boiling point the ketone is converted into a hydrocarbon of the composition $C_{14}H_{18}$; this compound has probably the constitution $CH_3 \cdot \langle \text{cyclohexane ring} \rangle \cdot C \begin{matrix} \nearrow CH_2 \cdot CH_2 \\ \searrow CMe \cdot CH_2 \end{matrix} \cdot CH_2$, but, as its further study had to be abandoned, we cannot put forward any very conclusive evidence in support of this view.

In the course of these experiments, laurobenzene

was also prepared in order to try and convert it into a hydrocarbon similar in constitution to that obtained from paraheptotoluene; this compound was also acted on by phosphoric anhydride but the hydrocarbon thus produced was not obtained in a state of purity.

Preparation of Heptoic Chloride.

Heptoic chloride is easily prepared by mixing the acid (100 grams) with the theoretical quantity of phosphorus pentachloride (160 grams), the application of heat not being required to complete the action. Care is necessary in distilling off the phosphorus oxychloride as, under ordinary atmospheric pressure, a considerable quantity of a black tarry residue may be produced if operating with large quantities. For this reason it is best to fractionate under a pressure of about 350 mm. at first; the portion passing over between 90 and 100° consists of almost pure oxychloride, but that collected between 100 and 130° contains a little heptoic chloride and is redistilled in a subsequent operation; as soon as the thermometer rises to about 130°, the pressure is lowered to about 90 mm., whereupon the remainder of the acid chloride passes over at 108—110° without bumping. The yield is about 95 per cent. of the theoretical.

Heptoic chloride is a moderately mobile oil, having an excessively disagreeable and irritating odour; it seems to be readily decomposed by water.

Paraheptotoluene, $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot [\text{CH}_2]_5 \cdot \text{CH}_3$.

For the sake of comparison with the ketone which, it was at first thought, had been produced from heptoic chloride alone, some paraheptotoluene was afterwards prepared by a simpler method, namely by treating pure toluene with heptoic chloride in presence of aluminium chloride, a reaction which has been previously employed by Krafft for the preparation of various ketones of this kind (*Ber.*, 1885, 19, 2982; 1887, 21, 2266).

Heptoic chloride (35 grams) was mixed in a large flask with a slight excess of the theoretical quantity of toluene, aluminium chloride (about 50 grams) added, and the flask connected with a reflux apparatus. Action commenced almost immediately at ordinary temperatures, and continued vigorously for about 5—8 minutes, after which time the evolution of hydrogen chloride slackened; the flask was then heated on a metal bath for about 20—25 minutes to complete the action. The dark brown product was allowed to cool, carefully treated with water, and the supernatant oil—which had partially solidified—extracted with ether; after washing well successively with sodium carbonate solution and water, the ethereal extract was dried,

the ether evaporated, and the residual oil distilled under the ordinary pressure; as soon as a small quantity of toluene had passed over, the thermometer rose at once to 297° , at which temperature practically the whole of the paraheptotoluene distilled as a pale yellow oil, which on cooling solidified to a mass of colourless crystals. The yield was about 90 per cent. of the theoretical.

This ketone was found to be identical with that obtained in the earlier experiments in which the impure "light petroleum" had been used; analyses of the first preparations gave the following results.

0.1590 gave 0.4792 CO_2 and 0.1463 H_2O . $\text{C} = 82.2$; $\text{H} = 10.2$.

0.1568 gave 0.4715 CO_2 and 0.1415 H_2O . $\text{C} = 82.0$; $\text{H} = 10.0$.

$\text{C}_{14}\text{H}_{20}\text{O}$ requires $\text{C} = 82.3$; $\text{H} = 9.8$ per cent.

Paraheptotoluene (hexyl paratolyl ketone) crystallises in colourless, waxy plates, melting at $42\text{--}43^{\circ}$; it dissolves freely in all ordinary organic solvents, and is best recrystallised from dilute alcohol or acetone. When a few drops of bromine are added to a solution of the pure ketone in dry chloroform, cooled to 0° , a brown coloration is produced, but no evolution of hydrogen bromide occurs; even after keeping for some time and then allowing the solution to evaporate at ordinary temperatures, the ketone is recovered unchanged; if, however, it be treated at ordinary temperatures with bromine without using a solvent, action takes place slowly, and a yellowish, oily, brown derivative is formed.

Paraheptotoluene is slowly oxidised by boiling dilute nitric acid, yielding a crystalline product which consists of a mixture of terephthalic and paratoluic acids; the terephthalic acid was identified by its characteristic properties, by analysis, and by conversion into its ethylic salt (m. p. $43.5\text{--}44^{\circ}$) and methylic salt (m. p. 138°); the paratoluic acid was not analysed, but it was identified by its ordinary properties and by the fact that it was converted into terephthalic acid on oxidation with alkaline potassium permanganate. The ketone is only very slowly oxidised by a boiling aqueous solution of potassium permanganate, but in this case the solid oxidation product consists only of terephthalic acid.

Paraheptotolueneoxime, $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NOH})\cdot[\text{CH}_2]_5\cdot\text{CH}_3$.

Before it had been ascertained that the ketone described above had been produced by the interaction of heptioic chloride and toluene, its oxime was prepared and treated with concentrated sulphuric acid; the substituted amide thus obtained was then hydrolysed with dilute sulphuric acid and the products examined. As these proved to be heptioic acid and paratoluidine, the substituted amide must have had the constitution $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot[\text{CH}_2]_5\cdot\text{CH}_3$,

and consequently the original ketone must have been paraheptotoluene.

The oxime was prepared by treating the pure ketone with hydroxylamine hydrochloride and excess of soda in aqueous alcoholic solution at the ordinary temperature; after evaporating the alcohol, the oily product was extracted with ether and the dried, filtered extract evaporated. A portion of the oil which had been kept over sulphuric acid under reduced pressure was analysed.

0.1591 gave 0.4400 CO₂ and 0.1434 H₂O. C = 75.4; H = 10.0.

0.1962 „ 10.8 c.c. of moist nitrogen at 16° and 765 mm. N = 6.75 per cent.

C₁₄H₂₁NO requires C = 76.71. H = 9.59; N = 6.39 per cent.

Paraheptotolueneoxime is a rather thick oil, insoluble or nearly so in water, but slightly soluble in potash; it dissolves freely in the ordinary organic solvents, and it interacts readily with acetic chloride with development of heat; it is also soluble in concentrated sulphuric acid.

Paraheptotoluidide, CH₃·C₆H₄·NH·CO·[CH₂]₅·CH₃.

The conversion of the oxime into the isomeric substituted amide was readily accomplished by warming it on the water bath with four times its weight of concentrated sulphuric acid for about 10 minutes; when the operation was continued much longer, the solution darkened, traces of sulphur dioxide were evolved, and the product was coloured. After pouring the solution into a large volume of water, the amide, which was first precipitated as an oil but rapidly solidified, was separated by filtration and recrystallised from alcohol.

0.1813 gave 0.5063 CO₂ and 0.1588 H₂O. C = 76.2; H = 9.7.

C₁₄H₂₁NO requires C = 76.7. H = 9.6.

Paraheptotoluidide crystallises from hot dilute alcohol in colourless, transparent, rather waxy plates, and from a mixture of ether and light petroleum in concentrically grouped needles; it melts at 78—79°, and dissolves freely in all ordinary organic solvents with the exception of light petroleum, in which it is only moderately easily soluble.

On hydrolysis with moderately concentrated (1 : 1) boiling sulphuric acid, paraheptotoluidide is resolved into its components, heptioic acid and paratoluidine; the base was identified by analysis by comparison with a sample of paratoluidine, and by converting it into acetoparatoluidide. Some paraheptotoluidide was also prepared by warming paratoluidine with heptioic chloride; this preparation was found to be identical with that obtained from the oxime of paraheptotoluene.

Hydrocarbon, C₁₄H₁₈.

It has already been mentioned that a hydrocarbon of the composition C₁₄H₁₈ may be obtained by heating paraheptotoluene with phosphoric anhydride; the following is the method employed.

The pure, dry ketone, in quantities of about 10 grams at a time, was heated to boiling in a flask provided with a reflux apparatus, and rather more than one molecular proportion of phosphoric anhydride gradually added, the contents of the flask being vigorously shaken after each addition in order to prevent the anhydride from caking at the bottom of the vessel; after boiling for about 25 minutes and then allowing to cool, the very dark mass was treated with water and submitted to distillation in steam. The oil in the distillate was separated, dried, and fractionated under ordinary atmospheric pressure; 41 grams of the crude product, which had been obtained from 60 grams of the ketone, yielded the following fractions:—Below 260° (5 grams), 260—265° (22 grams), 265—270° (8 grams), 270—278° (6 grams). The second and third fractions were again distilled, and finally a considerable quantity of an oil boiling constantly at 260—262° was obtained; this product was analysed with the following results.

0.1447 gave 0.4765 CO₂ and 0.1336 H₂O. C = 89.8; H = 10.2.

0.1443 „ 0.4728 CO₂ and 0.1310 H₂O. C = 90.0; H = 10.2.

C₁₄H₁₈ requires C = 90.3. H = 9.7.

This hydrocarbon was of a pale yellow colour, and showed a faint violet fluorescence, probably due to traces of impurity; it did not solidify when cooled to 0°, and was more mobile than the ketone from which it was derived; it had a faint odour recalling that of petroleum.

Several experiments were made in the hope of obtaining some evidence in favour of the constitutional formula suggested above, and although the results were by no means conclusive, they certainly indicated that the hydrocarbon was not an unsaturated compound of the constitution CH₃·C₆H₄·C:C·[CH₂]₄·CH₃. When, for example, the hydrocarbon was dissolved in chloroform, the solution cooled in a freezing mixture, and a cold chloroform solution of bromine cautiously added, a rapid evolution of hydrogen bromide set in long before one molecular proportion of the halogen had been run in, only the first few drops being immediately decolorised; the products obtained in various experiments of this kind, employing different quantities of bromine, did not crystallise, and were not analysed. Towards oxidising agents also, the hydrocarbon did not behave as if it contained an acetylenic linking as it was comparatively slowly acted on; when boiled with dilute nitric acid, it was converted into

terephthalic acid and a yellow, resinous product from which no definite compound was isolated; similar results were obtained on employing an alkaline solution of potassium permanganate.

Laurobenzene was easily prepared by treating lauric chloride with benzene and aluminium chloride under conditions similar to those employed in the case of paraheptotoluene; the lauric chloride used for this purpose contained phosphorus oxychloride, as it was found inexpedient to separate the whole of the latter owing to the darkening which occurred during the fractional distillation after about four-fifths of the oxychloride had passed over.

The dark product obtained after heating the benzene solution of the acid chloride with aluminium chloride until the evolution of hydrogen chloride was practically at an end was repeatedly treated with water to dissolve out the aluminium chloride and the pasty mass was then shaken vigorously with warm, concentrated potash; after allowing it to settle, the solution of potassium laurate was siphoned off from the semi-solid, supernatant layer of laurobenzene. This treatment having been repeated several times, the laurobenzene was dissolved in ether, the solution washed with potash and water successively, dried, and evaporated; the oily residue rapidly solidified, and, after having been spread on porous earthenware, was purified by recrystallisation from alcohol.

Laurobenzene crystallises in colourless, rather waxy plates melting at about 47° ; it is readily soluble in cold petroleum, ethylic acetate, and other organic liquids, but insoluble in water.

When laurobenzene was heated with phosphoric anhydride, it rapidly darkened, but, even after boiling it with a slight excess of the anhydride for about 20 minutes, only a part of it was converted into a hydrocarbon. The product, isolated by distillation in superheated steam, was a yellow oil which did not crystallise at 0° ; on fractional distillation, under ordinary pressure, it began to boil at about 325° , and the temperature then rose slowly to about 350° ; even after repeated fractionation, it still contained unchanged ketone, and gave unsatisfactory results on analysis.

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