

XXIV.—*Phenocycloheptene*.

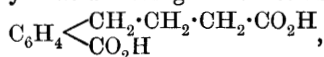
By FREDERIC STANLEY KIPPING and ALBERT E. HUNTER.

TAKING the conversion of hydrindamine hydrochloride, on heating, into the hydrocarbon indene and ammonium chloride (Kipping and Hall, *Trans.*, 1900, 77, 467) as an example of the ease with which aromatic cyclic hydrocarbons containing a partially reduced closed chain may be obtained from the corresponding saturated cyclic amines, it seemed highly probable that homologues of indene could be synthesised in a similar manner.

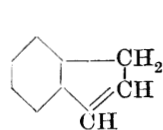
Moreover, as no hydrocarbon containing a benzene nucleus condensed with a seven-carbon ring, either reduced or partially reduced, has hitherto been prepared, the production of such a compound seemed to present an inviting subject for investigation, the results of which are here recorded.

When the dry hydrochloride of pheno- α -aminocycloheptane (Kipping and Hunter, *Trans.*, 1901, 79, 602) is heated at about 240°, it breaks up into ammonium chloride and an unsaturated hydrocarbon, a homologue of indene; the following equation, $C_{11}H_{13}NH_2 \cdot HCl = C_{11}H_{12} + NH_4Cl$, expresses this change.

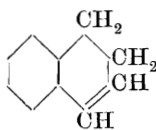
The unsaturated character of this hydrocarbon is established beyond a doubt by the ease with which it combines with bromine and by the readiness with which it is oxidised at the ordinary temperature by a dilute neutral solution of potassium permanganate; the position of the double binding is also established by the fact that the oxidation product is a dicarboxylic acid having the constitution



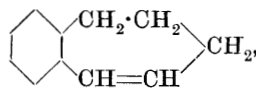
identical with the acid described by Roser (*Ber.*, 1885, 18, 3118). There is, therefore, little doubt that the hydrocarbon is a cyclic homologue of indene and of dihydronaphthalene, the series being indicated by the following formulæ:



Indene
(Phenocyclopentene).



Dihydronaphthalene
(Phenocyclohexene).



Phenocycloheptene.

and, in accordance with this view, we have named it *phenocycloheptene*.

This hydrocarbon displays a marked contrast to indene in its behaviour towards picric acid and towards benzaldehyde, for whereas indene readily forms with picric acid an additive compound which may be used for the identification of the hydrocarbon, *phenocycloheptene* does not give a like product; moreover, indene readily condenses with benzaldehyde in presence of a little sodium ethoxide, forming a well-defined compound, but *phenocycloheptene* cannot be made to undergo a similar condensation.

This difference in behaviour seems at first sight remarkable, considering the analogy between the constitution of indene and that of *phenocycloheptene*, but the explanation no doubt depends on the fact that the accumulation of methylene groups increases the aliphatic character of the compound. The non-formation of a picrate is thus accounted for, because, although a great many hydrocarbons containing a methenyl (CH_2) group afford picrates, others, such as the di- and tetra-hydrobenzenes, which contain methylene groups, do not appear to form such derivatives.

A similar difference in character has also been observed in the case of the two ketones, α -hydrindone and pheno- α -ketoheptamethylene, which correspond with the two hydrocarbons, indene and *phenocycloheptene* respectively; the former ketone is a solid melting at 44° , the latter is a liquid at the ordinary temperature; moreover, the oxime of α -hydrindone melts at 146° and the phenylhydrazone at 120° ; the oxime of pheno- α -ketoheptamethylene melts at $108\text{--}109^\circ$, whilst the phenylhydrazone, which does not crystallise at all well, decomposes with great rapidity. These differences indicate that the aliphatic character is more pronounced in the case of pheno- α -ketoheptamethylene than in that of α -hydrindone.

EXPERIMENTAL.

Distillation of Pheno- α -aminocycloheptane Hydrochloride.

When the pure dry hydrochloride, in quantities of about 5 grams, is carefully heated in a small Würtz flask, no change is observed until a temperature of about 240° is reached; the mass then partly liquefies; on heating more strongly, decomposition takes place, and a neutral oil distils over together with a little solid matter, leaving behind a white substance which sublimes on the cooler parts of the flask. The oil is dissolved in ether, the solution washed with water and dried with fused calcium chloride; the ether is then distilled off and the residue fractionated. In the first distillation, practically the whole of the liquid passes over between 231° and 234° , leaving a very small quantity

of residue; the portion boiling at 231—234°, when redistilled, yields a pure product having a boiling point of 233·5—234° (757 mm. pressure), the mercury thread being entirely immersed in the vapour.

In order to prove that the decomposition proceeds as in the case of hydrindamine hydrochloride, the sublimate was examined and was found to be ammonium chloride.

Phenocycloheptene, thus obtained, is a colourless, mobile, highly refractive liquid having a rather strong odour, recalling that of naphthalene or indene; its purity was established by the following analysis:

0·2107 gave 0·7071 CO₂ and 0·1570 H₂O. C = 91·5; H = 8·3.

C₁₁H₁₂ requires C = 91·6; H = 8·3 per cent.

In order to compare its density with that of its lower homologue, indene, specific gravity determinations were made with a freshly distilled sample boiling at 234°.

The weights of water and indene, at 4°, are 1·1444 and 1·1554 respectively, each weight being the mean of 5 determinations; the sp. gr. is 1·009 at 4°/4°.

The sp. gr. of synthetical indene, prepared in an analogous manner by Kipping and Hall (*loc. cit.*), is 1·008.

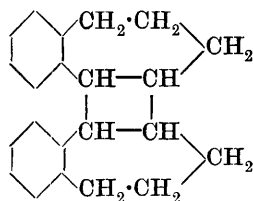
Action of Various Reagents on Phenocycloheptene.

A small quantity of the hydrocarbon does not furnish a picrate either on warming with picric acid or on mixing the two substances in benzene solution.

As indene readily condenses with benzaldehyde giving a crystalline derivative, C₆H₄ < $\begin{array}{c} \text{CHPh(OH)} \\ \text{CH} \end{array} \rangle \text{CH}$ (Marckwald, *Ber*, 1895, 28, 1500), it seemed desirable to see if phenocycloheptene would behave in a like manner.

This, however, does not seem to be the case, for if the hydrocarbon is warmed with benzaldehyde, even in the presence of a considerable quantity of sodium ethoxide, no reaction appears to take place, as no change in colour is observed and there is no development of heat; the product, moreover, does not solidify on standing.

On treatment with strong sulphuric acid at the ordinary temperature, the hydrocarbon passes into a pasty mass, which, on adding water, is precipitated as a heavy oil. As this product did not seem to crystallise at all readily, it was not investigated; possibly it is a condensation product having the following constitution:



Apparently, nearly the whole of the hydrocarbon is converted into this substance, and sulphonation, if it takes place at all, does so only to a limited extent.

Phenocycloheptene is not readily acted on by cold concentrated nitric acid, but on the addition of a little strong sulphuric acid nitration seems to occur, most of the hydrocarbon passing into solution; on subsequently diluting with water, a yellow solid is precipitated.

Oxidation of Phenocycloheptene with Potassium Permanganate.

In order to prove the existence of an ethylene linking in the seven-membered carbon ring of phenocycloheptene, the action of potassium permanganate was tried; it was found that a dilute neutral solution was readily reduced by a few drops of the hydrocarbon at the ordinary temperature even though the latter is practically insoluble in water.

Powdered potassium permanganate was added to the hydrocarbon suspended in water until the pink colour persisted, the solution being afterwards filtered and evaporated to a small bulk; on acidifying with hydrochloric acid, an acid was obtained which crystallised out, on cooling, in long, slender needles melting at 122° .

As under the above conditions the production of phenylbutyric-*o*-carboxylic acid, which is described by Roser (*loc. cit.*) as crystallising in plates melting at 138° , was expected, the oxidation product was recrystallised from water, dried over sulphuric acid, and analysed, the following result being obtained:

0.1188 gave 0.2764 CO_2 and 0.0598 H_2O . $\text{C} = 63.45$; $\text{H} = 5.58$.

$\text{C}_{11}\text{H}_{12}\text{O}_4$ requires $\text{C} = 63.4$; $\text{H} = 5.70$ per cent.

It thus appears from the analysis that oxidation has resulted in the production of phenylbutyric-*o*-carboxylic acid; this view of the composition of the acid being confirmed by an analysis of its silver salt:

0.056 gave 0.0285 silver. $\text{Ag} = 50.9$.

$\text{C}_{11}\text{H}_{10}\text{O}_4\text{Ag}_2$ requires $\text{Ag} = 51.2$ per cent.

The great difference in melting point and crystalline form between

our acid and Roser's was at first inexplicable, as in both cases the method of formation pointed emphatically to the constitution $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, and isomerism was out of the question. We therefore prepared phenylbutyric-*o*-carboxylic acid by Roser's method, namely, by heating together phthalic and succinic anhydrides in presence of anhydrous sodium acetate, and, after boiling the solution of the resulting anhydride, reducing the benzoylpropionic-*o*-carboxylic acid in sealed tubes by means of hydriodic acid and phosphorus; the reduced acid thus obtained crystallised from water in shining plates, melted at 138° , and was apparently quite different from that obtained by the oxidation of phenocycloheptene.

It was subsequently found, however, on crystallising the acid obtained by the oxidation of the hydrocarbon, that instead of giving needles melting at 122° it was deposited from water in plates melting at 138° .

The identity of this acid with the one obtained by Roser's method was then easily established; intimate mixtures, obtained by evaporating to dryness, aqueous solutions of the acids from the two sources in various proportions, were found to melt at the same temperature as the separate components, namely, at 138° .

These observations seemed to show that phenylbutyric-*o*-carboxylic acid is dimorphous, and further experiments confirmed this view, inasmuch as the acid obtained by the oxidation of the hydrocarbon, when crystallised from water, sometimes gave the needles melting at 122° and sometimes the less fusible plates.

Wishing to make a more complete investigation of the supposed dimorphism, we tried to convert the sample prepared by Roser's method into the modification melting at 122° , but were unsuccessful; moreover, on oxidising a further quantity of the hydrocarbon, we were unable to get the form melting at 122° , the acid persistently separating from water in plates melting at 138° , even when the solution was crystallised at temperatures ranging from 0° to about 100° .

The same result was obtained when the acid was crystallised from water containing hydrochloric acid or potassium chloride; although, unfortunately, we have not been able to arrive at any satisfactory explanation of our failure to determine the conditions which give the substance melting at 122° , our experiments show exclusively that the oxidation product of phenocycloheptene is identical with Roser's phenylbutyric-*o*-carboxylic acid.

Oxidation of Pheno- α -ketoheptamethylene with Nitric Acid.

In a previous paper (*ibid.*), we described the results of oxidising this ketone with nitric acid, and showed that *o*-phthalic acid was one of the products thus obtained. Having a further quantity of the

ketone at our disposal, we repeated the experiment under different conditions in order to obtain phenylbutyric-*o*-carboxylic acid, and thus confirm the conclusions arrived at from the results of the oxidation of the hydrocarbon with potassium permanganate. On boiling the ketone with very dilute (about 2—3 per cent.) nitric acid, practically the whole passes into solution, and after evaporating to a small bulk, filtering, and allowing to cool, an acid crystallises out in shining plates melting at 138° .

This product is sparingly soluble in cold water and agrees in physical properties with phenylbutyric-*o*-carboxylic acid prepared by Roser's method; moreover, on evaporating aqueous solutions of mixtures of the acids in varying proportions, homogeneous solids melting at 138° are obtained.

Action of Bromine on Phenocycloheptene.

In order to demonstrate further the unsaturated character of phenocycloheptene, we attempted to prepare a dibromo-additive compound by slowly adding the theoretical quantity of bromine, in dry chloroform, to the hydrocarbon in the absence of daylight; a considerable amount of heat was developed during the process, the product being well cooled from time to time; after the whole of the bromine had been added, the solution, which was colourless, was left for several hours. The chloroform was then distilled off, but on attempting to fractionate the residue it turned dark brown, and evolved hydrogen bromide as soon as the temperature reached about 80° ; even under a pressure of only 15 mm., considerable decomposition takes place, the separation of hydrogen bromide being accompanied by charring, so that only a small quantity volatilises as a thick, dark oil.

The additive compound, however, is volatile in steam, and is thus obtained in an almost colourless condition; it has then a strongly aromatic odour, and is heavier than water at the ordinary temperature. It does not solidify on cooling to 0° , whereas indene dibromide is a solid melting at 44° . Prolonged boiling with sodium carbonate solution has little or no effect on the dibromide, and digestion with dilute nitric acid apparently does not afford a crystalline oxybromide, the production of which might be expected from the ease with which indene dibromide yields a crystalline oxybromide under like conditions.

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