XC.—*Spinacene : its Oxidation and Decomposition.*

By A. Chaston Chapman.

SINCE the publication of my previous paper on spinacene (T., 1918, **113,** 458), I have been successful in obtaining a considerable quantity of the shark liver oil, and have prepared from it further and larger quantities of spinacene.

The more important physical properties of the hydrocarbon are recorded in the previous paper, but it seems desirable that the following results, obtained with a larger and purer specimen, should be recorded : $d_{20^\circ}^{20^\circ}$ 0·8588, $n_D^{20^\circ}$ 1·4951.

The specific refraction of the hydrocarbon calculated by the $(n^2 - 1)/(n^2 + 2)d$ expression is 0·3396, and the molecular refraction 134·5. Taking Conrady's average numbers for the atomic specific refractions (D-line), $C_{29}H_{48}$ with six ethenoid linkings requires $[R_L]$ 133·7.

I have also determined the heat of combustion in a Mahler bomb,

and obtained in two experiments, the numbers 4,388 and 4,372 molecular gram-calories, respectively.

Hydrogenation of Spinacene.—Since in my earlier experiments, the amount of spinacene available was small, and the saturated hydrocarbon was not obtained pure, I have prepared a further quantity. Dried hydrogen was passed as before through spinacene heated at about 200°, using active platinum black as the catalyst, and at the end of about fifty hours complete saturation was obtained. After the removal of the platinum, the resulting oil was distilled, when practically the whole boiled between 280—281° (corr.)/24 mm. The fraction so obtained was a colourless, slightly viscous liquid, completely devoid of odour (Found : C $= 85 \cdot 25$; H $= 14 \cdot 77$. $C_{29}H_{60}$ requires C $= 85 \cdot 29$; H $= 14 \cdot 71$ per cent.). It was optically inactive.

The density of the hydrocarbon at $15°/15° = 0 \cdot 8144$, and at $20°/20° = 0 \cdot 8119$. The value of $n_{D}^{20°} = 1 \cdot 4532$. Its specific refraction is therefore $0 \cdot 3330$, and its molecular refraction $135 \cdot 8$. The theoretical number for a saturated hydrocarbon having the formula $C_{29}H_{60}$ is $135 \cdot 5$.

Two determinations of the heat of combustion in the Mahler bomb gave 4,541 and 4,538 molecular gram-calories, respectively. The values recorded for the heats of combustion of carbon and hydrogen vary within somewhat considerable limits, but whichever results are taken the calculated value for the heat of combustion of a normal paraffin $C_{29}H_{60}$ would be considerably in excess of that found for the saturated hydrocarbon from spinacene, which is, of course, not a normal paraffin. This would appear to support the view of Fajans (*Z. physikal. Chem.*, 1921, **99**, 395) that saturated hydrocarbons with side chains have lower heats of combustion than the isomeric straight-chain compounds.

It also appears that the average thermochemical value for each of the six ethenoid linkings of spinacene is very near the value obtained for compounds of lower molecular weight. I propose the name *spinacane* for this saturated hydrocarbon as indicating its relationship to spinacene.

Spinacene Dodecabromide.—I have directed attention (*loc. cit.*) to the fact that not only were all the physical constants of spinacene in good agreement with the formula $C_{29}H_{48}$, but that, with one exception, the composition of the various compounds of this hydrocarbon was in better accord with that formula than with the formula $C_{30}H_{50}$ which I had previously been led to assign to it. The single exception to which I have referred was the dodecabromide. I did not, however, attach very great importance to this discrepancy inasmuch as the action of bromine on spinacene

is very complicated, and it seemed possible that the compound I had analysed might not have been entirely homogeneous. In order to clear up this point I have prepared a further and larger quantity of the dodecabromide in the manner already described.

When bromine is allowed to react with spinacene in ether solution, several successive crops of crystalline material can be obtained. In my earlier work, no steps were taken to separate the compound which crystallises out within, say, an hour of the addition of the bromine, from that which separates on standing for a longer time. In the present case, however, the crystalline material separating during the first hour was filtered off, washed with ether, and purified by repeated crystallisation from a mixture of tetrachloroethane and alcohol. The percentage of bromine rose from 70·0 in the original preparation to 70·88 after two recrystallisations, at which point it remained constant.

As $C_{30}H_{50}Br_{12}$ requires $Br = 70·07$ and $C_{29}H_{48}Br_{12}$ requires $Br = 70·79$, it will be seen that the dodecabromide contains almost exactly the amount of bromine required for the lower formula, and therefore comes into line with all the other compounds of spinacene. This experiment, therefore, removes the last remaining doubt as to the formula of the hydrocarbon.

Oxidation of Spinacene.—Many attempts were made to oxidise spinacene in the hope that products might have been obtained which would throw some light on its constitution. Among the oxidising agents chromic acid, potassium permanganate in acid and in alkaline solutions, potassium permanganate in acetone solution, nitric acid, oxygen in the presence of a catalyst, benzoyl peroxide, and hydrogen peroxide were tried.

An interesting point in connexion with these experiments was the remarkable stability shown by spinacene to the majority of the above oxidising agents, notwithstanding its highly unsaturated character. Thus, aqueous solutions of chromic acid appeared to have no effect on spinacene until their concentrations reached a point at which the destruction of the hydrocarbon occurred. The same behaviour was exhibited by permanganate, both in acid and in alkaline solutions. In the presence of alkali the permanganate acted more readily than in acid solution, and a little acetone together with a trace of some fragrant ketone was obtained. The great bulk of the hydrocarbon, however, remained either unacted upon, or was completely destroyed, according to the concentration of the permanganate. The addition of powdered potassium permanganate to an acetone solution of spinacene failed to give more encouraging results.

Action of Nitric Acid.—In a previous communication (*loc. cit.*),

I pointed out that with nitric acid spinacene appeared to undergo nitration and oxidation simultaneously. Fresh experiments have confirmed that observation, and have incidentally afforded a further example of the stability of the hydrocarbon. Spinacene can, in fact, be dissolved in a mixture of equal parts of strong sulphuric and nitric acids without any apparent decomposition or evolution of nitrous fumes, provided the temperature of the mixture be not allowed to rise too high during the addition.

On pouring the products of the reaction into water, a large yield of a yellow substance was obtained, very similar in its composition and general character to that obtained previously by the action of dilute nitric acid alone. Whether this consists of a single substance or a mixture of substances is not at present known.

Action of Benzoyl Peroxide.—When benzoyl peroxide was added to a solution of spinacene in glacial acetic acid, a vigorous reaction occurred on warming, and on pouring into an excess of ammonia a white amorphous oxidation product was obtained. Inasmuch as subsequent experiments showed that this was very similar in character to the product formed by the action of hydrogen peroxide, and as the latter method presented certain advantages, the benzoyl peroxide reaction was not further studied.

Action of Hydrogen Peroxide.—The strongest solutions of hydrogen peroxide commercially obtainable are without action on spinacene. In the absence of water, however, oxidation readily occurs. To a solution of 100 volume hydrogen peroxide sufficient acetic anhydride was added to react with the whole of the water present. This solution (230 c.c.) was added little by little to a hot solution of spinacene (35 c.c.) in glacial acetic acid (75 c.c.). An immediate reaction occurred with the development, as a rule, of sufficient heat to maintain the temperature of the liquid at the required point. Occasionally, however, it was found necessary to apply a little external heat. When the reaction following the addition of the last portion of the oxidising solution had subsided, the liquid was heated for about ten minutes, and the solution after cooling was then poured slowly into a solution of sodium hydroxide, containing considerably more alkali than was necessary to neutralise the whole of the acid. The precipitate which formed consisted of a white, amorphous substance. This was separated, washed as completely as possible with ice-cold water, and dried in an exhausted desiccator over sulphuric acid. The dried product was then ground, washed once more with ice-cold water, and dried as before to a constant weight.

As it was subsequently discovered that caustic alkali had some action on the oxidation product, a large volume of iced water was

substituted for the alkaline solution. This had the further advantage of yielding a more granular precipitate and one which could be more easily handled.

Three different preparations gave the following results : C = 64·8, 64·7, 64·9; H = 9·4, 9·4, 9·3. $C_{27}H_{48}O_8$ requires C = 64·8; H = 9·6 per cent. When this compound was dissolved in glacial acetic acid and again treated with hydrogen peroxide, it was recovered in a somewhat whiter condition, but its composition remained unaltered. It would appear, therefore, that this is a definite end product of the oxidation by this means.

Products containing less oxygen were isolated in some instances, but these were obviously mixtures with intermediate compounds. This substance is white, resinous, and insoluble in water. It has no sharp melting point, but begins to soften at about 40°, with decomposition. Owing to its marked tendency to form colloidal solutions, molecular weight determinations by the cryoscopic method were in all cases too high. In glacial acetic acid, for example, results indicating about 600 were obtained, but in benzene, in which the solutions were more markedly colloidal, results were obtained as high as 850. The formula given above requires $M = 500$. This behaviour is very similar to that observed in the case of attempts to determine the molecular weight of abietic acid in the above two solvents.

Having regard to the method of preparation of this substance, it was thought desirable to examine it for the presence of acetyl groups. These were found to be absent. It is saturated, and appears to be in the nature of an organic peroxide. The peroxide properties, however, are not very strongly marked since, although the compound liberates iodine from potassium iodide, the quantity so liberated is not sufficient to account for even one normally reacting peroxide group. In this respect it resembles many typical autoxidation products (Engler and Weissberg, " Vorgänge der Autoxydation ").

It would also appear to resemble very closely, if not to be identical with, the solid product formed when spinacene is exposed to air. Direct measurements showed that spinacene in these circumstances is capable of uniting with about 25 per cent. of its weight of oxygen. As in the case of linseed oil, however, volatile products are formed at the same time, so that the true oxygen absorption is really somewhat greater than that actually measured. Moureu and Dufraisse (*Compt. rend.*, 1922, **174**, 258) made the interesting observation that certain substances, notably quinol, even when present in traces, have the effect of preventing the atmospheric oxidation of certain unsaturated compounds. I

thought, therefore, it might be desirable to ascertain how spinacene would behave. When little more than a trace of quinol was added to spinacene, and the latter exposed to an atmosphere of oxygen, the weight remained practically constant, showing that there had been no absorption of oxygen. At the end of several months, the spinacene was as fluid as at the commencement of the experiment, whilst in a control experiment, the spinacene had become converted into a solid oxidation product at the end of a few weeks.

Although spinacene itself is very resistant to the action of most oxidising agents, the oxidation product above described readily undergoes further oxidation when treated with permanganate, especially in the presence of a little alkali. Thus, when it was treated gradually with an aqueous solution of potassium permanganate (1 per cent.) and vigorously shaken, oxidation readily occurred. When the reduction of the permanganate became slow, the oxides of manganese were filtered off, and the clear filtrate was concentrated and acidified with very dilute hydrochloric acid. A white, granular precipitate formed, which when washed and dried over sulphuric acid in an exhausted desiccator had the following composition (average of four closely agreeing analyses of four different preparations): $C = 65.62$; $H = 9.79$. $C_{25}H_{44}O_7$ requires $C = 65.78$; $H = 9.65$ per cent. This substance, which proved to be an acid, was prepared from a number of different preparations of the peroxide product, and the analytical results in all cases agreed very closely. It may, therefore, I think, be regarded as a definite compound. Its molecular weight was difficult to determine by the cryoscopic method, the results of several determinations ranging from 400 to 500. $C_{25}H_{44}O_7$ requires $M = 456$. Attempts to determine the molecular weight by titration with standard alkali tended to confirm the above molecular weight, but definite results were difficult to obtain owing to the fact that the acid is acted upon by an excess of alkali. When the peroxide oxidation product is allowed to stand in contact with aqueous alkali it undergoes decomposition with the formation of an acid, which could not, however, be obtained in a condition pure enough for analysis.

Decomposition of Spinacene by Heat.—The results obtained by distilling spinacene under a pressure of about 45 mm. in the presence of a small quantity of metallic sodium have been described (*loc. cit.*), and this experiment has been repeated. As before, a great deal of polymerisation occurred, but the main product distilling over consisted of a *cyclo*dihydroterpene, having properties closely agreeing with those of the compound previously described. Many attempts were made under varying conditions to prepare a definite bromine

derivative of this hydrocarbon, but in every case an oil was obtained from which crystals did not separate even on long standing. Inasmuch as the sodium appeared to bring about so much polymerisation, I endeavoured to secure decomposition of the spinacene by heat in another manner. To this end, the spinacene was distilled from a Wurtz flask with a long and wide neck. In this neck there was suspended a small grid of fine platinum wire which could be kept at any required temperature by means of an electric current. In this apparatus the spinacene could be distilled under any required pressure and the vapours compelled to pass over the heated platinum surface. In practice, it was found best to maintain the pressure in the flask at about 45 mm. and to keep the platinum grid at a dull red heat throughout the experiment. A U-tube containing high-boiling liquid paraffin, and surrounded by a freezing mixture, was introduced into the condensing system after the ordinary water condensers, and arrangements were also made for collecting gaseous products.

The product, condensed by the water condenser, consisted of a yellow, mobile liquid, more than half of which was found to be distillable with steam, the remainder consisting chiefly of unchanged spinacene. The steam-distilled portion was submitted to fractional distillation under reduced pressure, and was found to consist almost entirely of a substance boiling at 79—83°/33 mm. (Found : $C = 86.7$; $H = 13.2$. $C_{10}H_{18}$ requires $C = 87.0$; $H = 13.0$ per cent.). This hydrocarbon consists of a yellow liquid having a smell strongly suggestive of the lower olefines. Inasmuch as the yellow colour persists after steam distillation and other methods of purification, it would appear to be a constitutional property. The possibility, however, of the presence of a small proportion of some highly coloured hydrocarbon is not entirely excluded. It boils at 160—167°/750 mm., the liquid becoming discoloured, and ultimately viscous owing to polymerisation. It is optically inactive.

A molecular-weight determination in benzene gave the following results : 0.4683 in 13.568 benzene gave $\Delta t = - 1.265°$. $M = 136$. $C_{10}H_{18}$ requires $M = 138$. It has $d_{15°}^{15°}$ 0.8025 and $d_{20°}^{20°}$ 0.8008, $n^{15°}$ 1.4606 and $n^{20°}$ 1.4584. Its specific refraction, calculated by the n^2 formula, is 0.341, and the molecular refraction 47.1. Taking Conrady's average numbers for the atomic specific refractions (D-line), $C_{10}H_{18}$ with two ethenoid linkings requires 47.5.

A determination of the amount of iodine with which this compound is capable of uniting gave a value of 347, the theoretical number for $C_{10}H_{18}$ with two ethenoid linkings being 368 parts per cent.

Bromine absorption estimations were also made, and it was found in a number of experiments that the values corresponded

with an addition of between three and four atoms of bromine for each molecule of the hydrocarbon. It will be seen, therefore, that this hydrocarbon has the properties of a diolefine, whilst the hydrocarbon obtained by heating spinacene in the presence of sodium is a *cyclo*-compound of the same molecular formula. The bromine estimations, as well as the other results, appear to indicate that it is not easy to obtain either of these two compounds in a quite pure condition, but that each is very apt to contain a little of the other. There can, I think, be very little doubt that they are closely related, but attempts to convert the olefinic hydrocarbon into the *cyclo*-compound have not, so far, been successful.

Bromine Derivative.—The hydrocarbon was dissolved in five times its weight of a mixture of ether (4 parts) and amyl alcohol (1 part). A solution of bromine in the same mixed solvent was added slowly, and the liquid kept cool in a freezing mixture. After standing for twelve hours, the greater part of the solvent was allowed to evaporate at the ordinary temperature. When the remaining liquid was allowed to stand, crystals formed slowly and after a time a dense oil separated. The yield of this crystalline compound was very small, and whether crystals are obtained or not appears to depend very much upon the precise conditions under which the experiment is carried out. The colourless crystals obtained by recrystallising from a mixture of ether and amyl alcohol and drying to constant weight in an exhausted desiccator over sulphuric acid melted at $136°$ (corr.) (Found : $Br = 69·64$. $C_{10}H_{18}Br_4$ requires $Br = 69·87$ per cent.).

A molecular-weight determination in benzene was made :

$0·1904$ in $10·6917$ benzene gave $\Delta t = -0·195°$. $M = 456$. $C_{10}H_{18}Br_4$ requires $M = 458$.

In the fractional distillation of the products from which this olefinic hydrocarbon was obtained there occurred a small fraction, boiling under atmospheric pressure between $40°$ and $50°$, and on distilling the high boiling paraffin, used for trapping low-boiling compounds formed during the decomposition of the spinacene by heat, a larger quantity of a fraction, boiling within the same range of temperature, was obtained.

On further distillation, this was resolved into two fractions, one boiling under atmospheric pressure at $40—45°$, and the other at $45—50°$. These had $d_{20°}^{20°}$ $0·6800$ and $0·6846$, respectively, and $n_D^{15°}$ $1·4170$ and $1·4186$. The specific refraction of the lower of the two fractions (b. p. $40—45°$), calculated by the n^2 formula, $= 0·371$. The calculated specific refraction of isoprene $(C_5H_8) = 0·360$, and of amylene $(C_5H_{10}) = 0·354$.

As neither of these fractions appeared to consist of a single

compound, and as the physical properties and the numbers given on analysis were very similar, it was decided to mix them together for purposes of further examination. The following are the results of analyses (Found : $C = 87 \cdot 20$, $87 \cdot 19$; $H = 13 \cdot 20$, $13 \cdot 20$. C_5H_8 requires $C = 88 \cdot 2$; $H = 11 \cdot 8$. C_5H_{10} requires $C = 85 \cdot 7$; $H = 14 \cdot 3$ per cent.).

A molecular-weight determination in benzene gave the following results :

$0 \cdot 1955$ in $13 \cdot 799$ benzene gave $\Delta t = - 0 \cdot 948°$. $M = 74$. (C_5H_8 requires $M = 68$. C_5H_{10} requires $M = 70$).
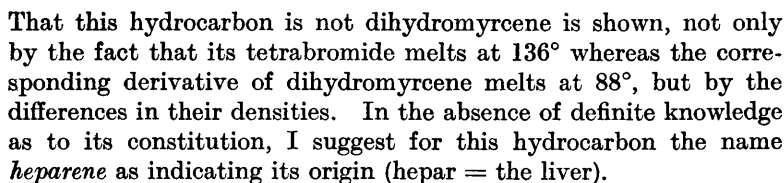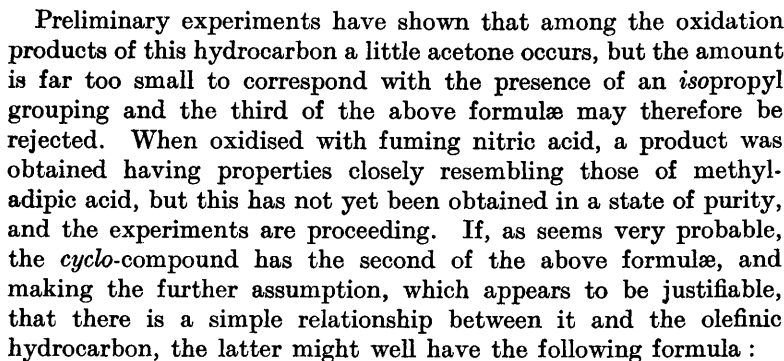
A determination of the iodine absorption by the Wijs method gave a value of 344, the theoretical number for C_5H_{10} with one ethenoid linking being 362. The calculated value for isoprene, on the other hand, is 741, but it has recently been shown by Faragher, Gruse, and Garner (*J. Ind. Eng. Chem.*, 1921, **13**, 1044) that the number actually obtained with isoprene by the Wijs method is 382. The iodine value is not, therefore, very conclusive in regard to the presence or absence of some C_5H_8 hydrocarbon in this fraction. These results appear to indicate that this fraction consists of one or more of the amylenes with a proportion of some C_5H_8 hydrocarbon, probably isoprene.

In addition to the above substances formed during the decomposition of spinacene by heat, a certain amount of gas was collected. This gas, on analysis, was found to contain about 75 per cent. of unsaturated (olefinic) and about 25 per cent. of saturated (paraffin) hydrocarbons. The composition, however, varied somewhat according to the precise conditions of the experiment.

Of the two $C_{10}H_{18}$ hydrocarbons resulting from the decomposition of spinacene by heat, the *cyclo*-form, at least, has undoubtedly been obtained in a nearly pure condition. For purposes of identification, therefore, considerable reliance may safely be placed upon the correctness of its physical properties as recorded in my previous communication. In that communication I expressed the opinion that this hydrocarbon might prove to be *cyclo*dihydromyrcene or *cyclo*linaloolene. Recent work has shown that these two hydrocarbons may be identical, but whether that is the case or not, the hydrocarbon obtained from spinacene differs from either, since it does not yield any lævulic acid or other keto-acid on oxidation.

On the other hand, its physical properties agree very closely with those assigned by Wallach (*Annalen*, 1908, **360**, 34) to certain *cyclo*hexane derivatives containing a semi-cyclic double linkage.

The following are three of the compounds of this series, together with their chief physical properties, which the hydrocarbon from spinacene most closely resembles. Under (4) I have given, for

purpose of comparison, the corresponding numbers for the spinacene hydrocarbon :

(1)	(2)	(3)	(4)

B.p. ... 170—173°	172—174°	173—175°	170—175°
D. ...... 0·814 at 19°	0·815 at 19°	0·825 at 21°	0·813 at 20°
M_D ... 46·35	46·28	46·25	46·31
M_D (calc.) 45·8	45·8	45·8	45·8

Preliminary experiments have shown that among the oxidation products of this hydrocarbon a little acetone occurs, but the amount is far too small to correspond with the presence of an *iso*propyl grouping and the third of the above formulæ may therefore be rejected.   When oxidised with fuming nitric acid, a product was obtained having properties closely resembling those of methyl-adipic acid, but this has not yet been obtained in a state of purity, and the experiments are proceeding.   If, as seems very probable, the *cyclo*-compound has the second of the above formulæ, and making the further assumption, which appears to be justifiable, that there is a simple relationship between it and the olefinic hydrocarbon, the latter might well have the following formula :

$$CH_3—C\begin{smallmatrix}CH_2\\CH_2\end{smallmatrix} \begin{smallmatrix}CH_3\\CH_2\end{smallmatrix}C{=}CH{\cdot}CH_2{\cdot}CH_3.$$

That this hydrocarbon is not dihydromyrcene is shown, not only by the fact that its tetrabromide melts at 136° whereas the corresponding derivative of dihydromyrcene melts at 88°, but by the differences in their densities.   In the absence of definite knowledge as to its constitution, I suggest for this hydrocarbon the name *heparene* as indicating its origin (hepar = the liver).

Constitution of Spinacene.

Of the products obtained from spinacene when decomposed by heat as described in this paper, from 45—50 per cent. consists of the olefinic hydrocarbon heparene.   From this it is highly probable that the spinacene molecule contains two of these $C_{10}H_{18}$ complexes.   That being the case, the constitution of spinacene may be provisionally represented in the following manner :
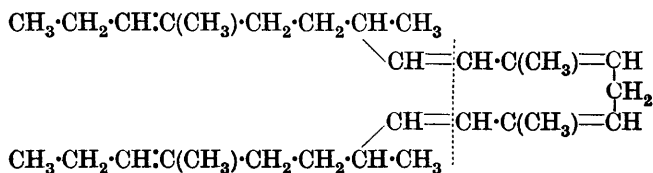
The above formula is not intended to represent anything more than an outline of the structure of spinacene, but it appears to explain satisfactorily the properties of that hydrocarbon so far as these are at present known.

Certain of the properties of spinacene might, perhaps, be more readily explained by an alternative formula with two terminal unsaturated *iso*propyl groupings, but although such a formula is not entirely excluded it is, in my opinion, less probable than the one I have given above.

In conclusion, I desire to express my best thanks to Mr. J. J. Scanlan, A.R.C.Sc.I., A.I.C., for much valuable help in connexion with this investigation.