52. *Infra-red Studies of Retene and its Hydrogenation Products.*

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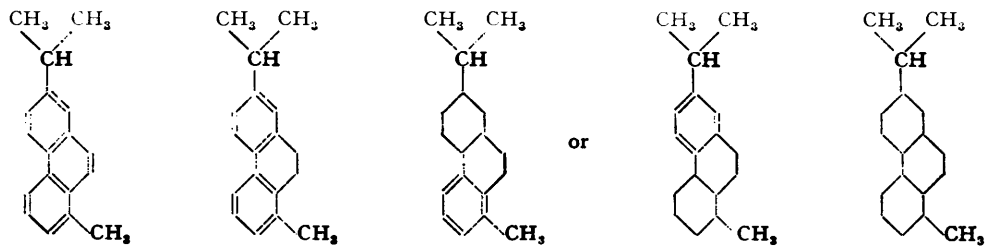
The infra-red absorption spectra of retene, dihydroretene, octahydroretene, and perhydroretene have been measured, between 3 and 15 μ. They have been used to provide analytical methods of studying the nature of the products formed in the hydrogenation of retene by different methods. It has been found that these products are confined to dihydro-, octahydro- and perhydro-retene, and this corresponds to the stability of these compounds in which only aromatic and fully saturated rings occur. Similar reactions involving the catalytic dehydrogenation of hydroretenes have been examined. A melting-point diagram is given for retene and dihydroretene, which form a complete series of mixed crystals.

The presence of the phenanthrene nucleus in such important classes of compound as the sterols, bile acids, and certain alkaloids has prompted further work on naturally occurring polynuclear aromatic compounds and their derivatives.

Retene [1-methyl-7-*iso*propylphenanthrene (I)] is of particular interest in relation to the resin acids and the diterpenes. It can theoretically form seven hydroretenes, in which 2, 4, 6,



(I.) (II.) (III.) (IV.)

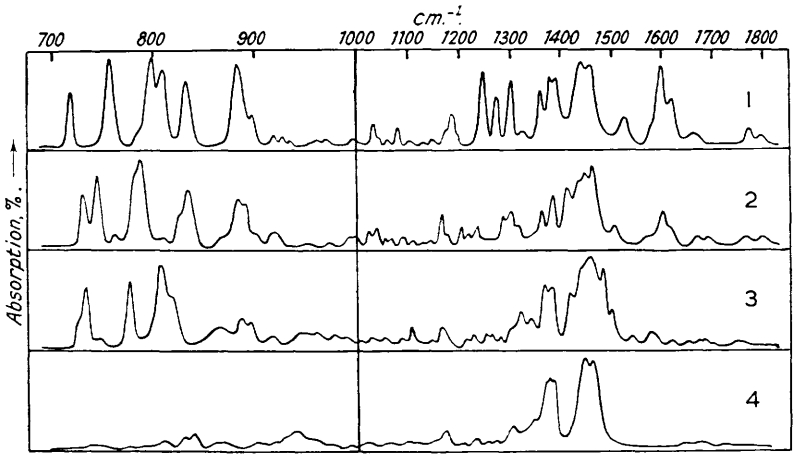
8, 10, 12, and 14 hydrogen atoms respectively have been added to the molecule. Retene and perhydroretene can each exist in only one form, but all the others are capable of structural isomerism. For example, there are theoretically 16 isomers of dihydroretene, depending on which bond has been saturated, and with the more fully hydrogenated derivatives the number of isomers is still greater. On theoretical grounds, the isomers may differ greatly in stability, and in practice dihydroretene is found only as the 9 : 10-compound (II), formed from retene either by catalytic reduction or by the action of sodium and amyl alcohol. On grounds of ring strain, the most stable derivatives would be expected to be dihydroretene, octahydroretene (III), and perhydroretene (IV). These derivatives should be formed preferentially in the catalytic reduction of retene. It has been shown, for example, that reduction of retene in presence of a nickel catalyst gives perhydroretene (Ipatiev, *Ber.*, 1909, **42**, 2095; Laakso, *Ann. Acad. Sci. Fennicæ*, 1949, *A*, No. 28), whilst if copper chromite is used a mixture of dihydroretene and octahydroretene is formed (Laakso, *loc. cit.*). Whenever the hydrogenation with a nickel catalyst is interrupted before the full complement of hydrogen has been taken up, a mixture of these particular hydroretenes and retene is obtained. Thus, if the equivalent of four hydrogen atoms has been absorbed, no tetrahydroretene is found but only retene and perhydroretene.

However, Bamberger and Lodter (*Ber.*, 1887, **20**, 3073) claimed to have prepared tetrahydroretene using sodium and amyl alcohol. Liebermann and Spiegel (*Ber.*, 1889, **22**, 779) similarly claimed to have prepared dodecahydroretene using phosphorus and hydrogen iodide, and Virtanen a whole series of hydroretenes by the same methods (*Ber.*, 1920, **53**, 1880). In these investigtions no chemical tests were given which characterised the products, which might have been mixtures. It therefore seemed appropriate to apply infra-red absorption spectroscopy to the problem, and the results have indeed substantiated the argument outlined above about the relative stability of the hydroretenes. Some analogous problems involved in the dehydrogenation of hydroretene have been examined by the same method.

The spectrometers used were automatic recorders, described in detail elsewhere (Thompson and Whiffen, *J.*, 1945, 269; Richards and Thompson, this vol., p. 124). A rock-salt prism was used for most of the work, but the region 2—7 μ. was also measured with prisms of calcium fluoride and lithium fluoride. The compounds were measured as thin solid layers melted on rock-salt plates, as liquids, or in dilute solutions in carbon tetrachloride or bromoform as indicated below.

The Hydrogenation of Retene.—The spectra of pure samples of retene, dihydroretene, octahydroretene, and perhydroretene were first determined for reference. These are shown in Figs. 1 and 2.

FIG. 1.



(1) *Retene, solid film.* (2) *Dihydroretene, solid film.* (3) *Octahydroretene, liquid.* (4) *Perhydroretene, liquid.*

Part of the spectrum of retene was previously recorded by Barnes, Gore, Liddel, and Williams (*Ind. Eng. Chem. Anal.*, 1943, **15**, 659). It is seen that well-marked differences exist between the spectra in several spectral regions, which serve to characterise the compounds, and it seems certain that other hydroretenes would have equally distinctive features.

Attempts were then made to prepare tetrahydro-, hexahydro-, octahydro-, and decahydroretene by the methods described by Virtanen. For tetrahydro-retene, retene was reduced by sodium in amyl alcohol in several ways, namely, (*a*) with a small amount of sodium and heating with an open flame, (*b*) with a larger amount of sodium and similar heating, (*c*) with a further excess of sodium, and (*d*) with an excess of sodium but heating in an oil-bath. The spectra of the products, and of distillation fractions from each of them, were then measured. In the first three cases, a moderately strong band, the originator of which appeared to become concentrated in the higher-boiling fractions, occurred at 1740 cm.$^{-1}$ and was attributed to a carbonyl group. This did not occur with material obtained by method (*d*) in which local over-heating was avoided, and the compound responsible for it, which could not have been present in great amount, can be confidently regarded as a by-product formed from amyl alcohol. All the other bands in the spectra could be satisfactorily accounted for as a mixture of two or more of those of retene, dihydroretene, and octahydroretene.

The more saturated hydroretenes were made by reduction of retene with phosphorus and

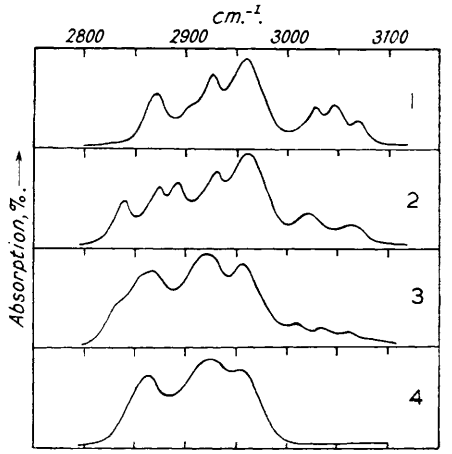
hydrogen iodide. In this case all the bands found in the spectra of the products were explicable in terms of retene, dihydroretene, octahydroretene, and perhydroretene. As the proportion of hydrogen taken up is increased, the more fully hydrogenated derivatives become more prominent, as might be expected.

It was found that the boiling point of the mixture of hydrogenation products did not vary gradually and continuously during a distillation, and this suggested the formation of azeotropic mixtures. It will be shown later that retene and dihydroretene form a complete series of mixed crystals.

Dehydrogenation of Hydroretenes.—When a sample of dihydroretene, which had been prepared by catalytic reduction of retene and purified by recrystallisation, was dehydrogenated with Raney nickel, it did not evolve the full equivalent of hydrogen, but about 10% less (Laakso, *Ann. Acad. Sci. Fennicæ*, 1949, *A*, No. 32). It had been suggested that this result might have arisen by disproportionation. The spectral examination of the sample of dihydroretene showed however that it contained a small amount of retene. By repeated recrystallisation, it was possible to prepare a specimen of dihydroretene, m. p. 56—58°, the spectrum of which was free from the bands of retene. Dihydroretene was found to become

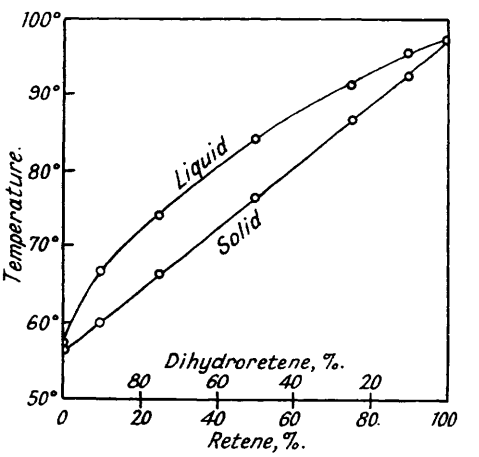
FIG. 2.

Solutions in carbon tetrachloride.



(1) *Retene*, 2%. (2) *Dihydroretene*, 2%.
(3) *Octahydroretene*, 2%.
(4) *Perhydroretene*, 1%.

FIG. 3.



concentrated in the mother-liquor rather than in the crystals, and the purest specimen was found in the last mother-liquor after fractional evaporation and filtration of the alcoholic solution. Retene and dihydroretene appear to form a complete series of mixed crystals, the melting point increasing as the percentage of retene increases (Fig. 3). The presence of retene in the sample of dihydroretene would account for the deficit of hydrogen in the dehydrogenation discussed above. Indeed, the gradual melting over 2° of the sample of dihydroretene thought to be pure suggests that about 1% of impurity may still be present, but the spectra show definitely that this impurity cannot be retene.

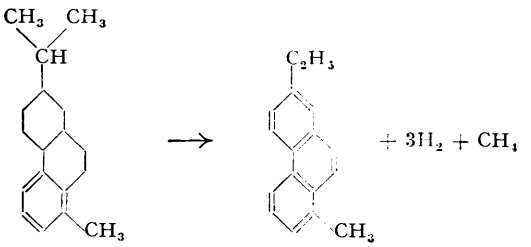
Simultaneously with the liberation of hydrogen in the dehydrogenation process, methane is formed. This presumably comes from a degradation of the *iso*propyl group, but spectral changes which might confirm this would be slight and have not been detected.

The dehydrogenation of octahydroretene has also been studied. With Raney nickel at 220° a smooth reaction occurs in which hydrogen is liberated, but in smaller amount than would be required for complete dehydrogenation. At the same time much methane is formed. These results can be explained by the occurrence of two reactions simultaneously with the straight dehydrogenation.

In the first, disproportionation leads to retene and perhydroretene :

$$2C_{18}H_{26} \longrightarrow C_{18}H_{18} + C_{18}H_{32} + H_2$$

and in the second, the *iso*propyl radical loses methane, subsequent dehydrogenation leading to 1-methyl-7-ethylphenanthrene :



The product obtained from the dehydrogenation of octahydroretene was found spectroscopically to show bands of retene and perhydroretene, and also other unexplained bands. The sample was then separated into a crystalline and an oily fraction. The former was almost pure retene; the latter contained much perhydroretene and also the unidentified component. Although the third component could not be completely identified from its spectral features, there is no doubt that it contains aromatic nuclei and methyl groups. It has not yet been possible to obtain a synthetic sample of 1-methyl-7-ethylphenanthrene to establish the expected identity.

Experimental.

Retene.—The retene used in these experiments was prepared, from the higher fractions of tar, by distillation and fractional distillation (Talvitie and Laakso, *Ann. Acad. Sci. Fennicæ*, 1946, *A*, No. 21, 10). The m. p. of the pure sample was 98—98·5°.

Dihydroretene.—The dihydro-compound was prepared by the reduction of retene with sodium in amyl alcohol (Virtanen, *loc. cit.*). The infra-red spectrum showed that the product still contained retene, but a retene-free sample, m. p. 56—58°, was isolated from the mother-liquor. A better method for the preparation of pure dihydroretene is to use more sodium, under slightly modified conditions.

10 G. of retene were dissolved in 100 c.c. of dry amyl alcohol and heated in an oil-bath at 130°. 8 G. of sodium were added during 2 hours. When all the sodium had dissolved the reaction mixture was poured into water, and the amyl alcohol layer separated and washed with water until it was neutral. Amyl alcohol was distilled off in steam, and the residual mixture of hydroretenes kept at −10° overnight. The crystals formed were filtered off and recrystallised twice from alcohol. The resultant dihydro-compound had m. p. 56—58°, and was shown by its infra-red spectrum to contain no trace of retene.

Octahydroretene.—This was prepared by catalytic reduction of retene with a copper chromite catalyst (Laakso, *Ann. Acad. Sci. Fennicæ*, 1949, *A*, No. 28). It was a pale yellow, very viscous oil, b. p. 191—192°/1·0 mm.

Perhydroretene.—This hydrocarbon was prepared by the catalytic reduction of retene with a nickel–kieselguhr catalyst (Laakso, *loc. cit.*). It was a colourless, not very viscous, oil, b. p. 332—335°/760 mm.

Preparation of "Tetrahydroretene."—(a) *With direct heating.* A solution of 10 g. of retene in 75 c.c. of amyl alcohol was heated to boiling on a wire-gauze, and 9 g. of sodium, cut into small pieces, were added during 2 hours. The mixture was poured into water, the amyl alcohol layer was separated, the solvents were removed by distillation, and "tetrahydroretene" was isolated as described by Virtanen, as a yellowish viscous oil, b. p. 180—183°/10 mm.

(b) *With excess of sodium and direct heating.* 10 G. of retene in 400 c.c. of amyl alcohol were heated to boiling on a wire-gauze. 25 G. of sodium, cut in small pieces, were added during 3 hours. Subsequent treatment was as in (a) above, three different fractions being collected during distillation under reduced pressure.

(c) *With excess of sodium and indirect heating.* The procedure was the same as in (b), but the flask was placed in an oil-bath heated to 130°. The product was distilled *in vacuo* three times, and two main fractions were taken. The first fraction (2·5 g.), b. p. 190—195°/1·0 mm., a yellow, viscous oil, was pure octahydroretene (Found : C, 89·5; H, 10·6. Calc. for $C_{18}H_{26}$: C, 89·2; H, 10·8%). The second fraction (3·0 g.), b. p. 220—223°/10 mm., a yellow viscous oil, gave analytical data corresponding to tetrahydroretene (Found : C, 90·5; H, 9·3. Calc. for $C_{18}H_{22}$: C, 90·7; H, 9·3%).

Reduction of Octahydroretene with Sodium.—5 G. of octahydroretene were dissolved in 100 c.c. of amyl alcohol and heated at 130° in an oil-bath. 10 G. of sodium, in small lumps, were added during 2 hours. Subsequent treatment, as in (a) above, gave 4 g. of a product, b. p. 190—195°/1·0 mm., which was a viscous, yellow oil, identical with the original sample of octahydroretene.

Preparation of "Hexahydroretene."—6 G. of retene, 7 g. of hydrogen iodide, and 3 g. of red phosphorus were heated in an atmosphere of carbon dioxide, in a sealed tube, so that the temperature rose to 200° during 3 hours. The tube was maintained at this temperature for 10 hours as described by Virtanen (*loc. cit.*). The product was boiled with water and extracted with ether, the ethereal extract was washed with water and dried (Na_2SO_4), the ether was evaporated, and the residue was distilled *in vacuo*. The fraction, b. p. 175—177°/10 mm., was collected, and its analysis found to correspond to that for "hexahydroretene" (Found : C, 90·1; H, 10·2. Calc. for $C_{18}H_{24}$: C, 89·9; H, 10·1%).

Preparation of Octahydroretene.—The procedure was the same as above, but the temperature was raised to 240° during 4 hours and was maintained at that level for 10 hours. The fraction, b. p.

163—165°/10 mm., was collected: its analysis corresponded to that of octahydroretene (Found: C, 89·1; H, 10·7. Calc. for $C_{18}H_{26}$: C, 89·2; H, 10·8%).

Preparation of Decahydroretene.—The procedure was again as above, but the temperature was raised to 285° during 4 hours and maintained for 10 hours. The fraction, b. p. 155—158°/750 mm., was collected and gave an analysis corresponding to decahydroretene (Found: C, 88·7; H, 11·2. Calc. for $C_{18}H_{28}$: C, 88·5; H, 11·5%).

Dehydrogenation of Dihydroretene.—1 G. of dihydroretene, m. p. 64—65°, and 0·3 g. of Raney nickel were heated, in a distillation flask connected to a gasometer, on an oil-bath at 220° until the evolution of gas had ceased. The dehydrogenation product was dissolved in ether and separated from the catalyst by filtration. It had m. p. 89—91°, raised by recrystallisation to 98—99°.

Dehydrogenation of Octahydroretene.—(a) *Incomplete dehydrogenation.* 1 G. of octahydroretene, b. p. 191—193/10 mm., and 0·3 g. of Raney nickel were similarly heated, until about 200 c.c. of gas had been evolved (corresponding to about 2 moles of hydrogen). The dehydrogenation product was dissolved in ether and separated from the catalyst by filtration.

(b) *Complete dehydrogenation.* 10 G. of octahydroretene, b. p. 191—193°/10 mm., and 3 g. of Raney nickel were similarly heated until the evolution of gas had ceased. The dehydrogenation product was separated from the catalyst by filtration when hot, and, on cooling, divided into a crystalline and an oily part. The crystals, m. p. 98—99°, were almost pure retene; the oily part was divided into two fractions of different boiling point and their infra-red spectra examined.

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[*Received, June 30th,* 1949.]