300. *The Application of Infra-red Analysis to the Study of the Reaction of Certain Olefins with Hydrogen Sulphide.*

By N. SHEPPARD and G. B. B. M. SUTHERLAND.

The method of infra-red analysis has been used to investigate the reaction of geraniolene and dihydromyrcene with hydrogen sulphide in the presence of catalysts that usually promote "normal" addition to the double bond according to the Markovnikov rule. It has been possible to show conclusively that under these conditions both the hydrocarbons give mono-addition products which consist partly of cyclic sulphides, geraniolene giving rise to 2 : 2 : 6 : 6-tetramethyltetrahydrothiopyran, and dihydromyrcene to 2 : 2 : 6-trimethyl-6-ethyltetrahydrothiopyran. Such products could only have been formed by "normal" addition reactions. The products of the reaction of hydrogen sulphide with dihydromyrcene under conditions favouring "abnormal" addition gave very different spectra.

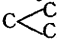
In order to apply the infra-red method it was necessary first to establish rules for the spectroscopic identification of certain hydrocarbon groups. These rules are briefly discussed.

In the preceding paper Naylor has described an investigation of the reaction of hydrogen sulphide with the hydrocarbons geraniolene and dihydromyrcene. Many of the conclusions relating to the structures of the reaction products came from an investigation of their infra-red spectra. The purpose of this paper is to present in detail the evidence for these conclusions.

Infra-red analysis can be used in two ways to establish the structure of a reaction product. In the first place, any chemical bond or group that has characteristic infra-red absorption bands can be detected, and while in most cases this does not establish the structure it may enable one to eliminate some of the possible formulations and give strong presumptive evidence for a particular one. The second and more conclusive method is to compare the spectrum of the reaction product with that of a specially synthesised specimen of the compound postulated as the reaction product. Both methods have been used in the present investigation, the first two sections of which are concerned with the material required for the first method, while the third contains the combined application of both methods to the problem in hand.

Chemical Groupings and their Characteristic Absorption Bands.—The various characteristic group frequencies that we shall use in the examination of the reaction products are given in Table I, where R represents an alkyl group. Most of these correlations are well established (see, *e.g.*, Herzberg, "Infra-red and Raman Spectra of Polyatomic Molecules," Van Nostrand Co. Inc., 1946; Barnes, Gore, Liddel, and Williams, "Infra-red Spectroscopy," Reinhold, 1944; Thompson and Torkington, *Trans. Faraday Soc.*, 1945, **41**, 246), but those marked with an asterisk, which are more precise characterisations of older correlations, have recently been established in this laboratory and full details will be published elsewhere.

TABLE I.

Chemical grouping.	Type of vibration.	Frequency in cm.$^{-1}$.
SH	SH valence	2500—2650
CH_2 and CH_3	CH deformation	1430—1470
CH_3	CH deformation	1370—1375
 $C<^{CH_3}_{CH_3}$	CH deformation	*ca.* 1360 and 1380 *
$RR'C{:}CH_2$	C=C valence	1645—1655 *
$RR'C{:}CH_2$	CH deformation	885— 895
$RR'C{:}CHR''$	C=C valence	1670—1680 *
$RR'C{:}CHR''$	CH deformation	800— 840

Both the C=C valence and the C—H deformation absorptions of the disubstituted ethylenes have considerably higher extinction coefficients than the corresponding absorptions of the trisubstituted compounds. This is important if such absorptions are used to estimate the relative amounts of the two types of grouping in a mixture of both.

The Spectra of the Olefins.—The two hydrocarbons originally used for the reaction with hydrogen sulphide were geraniolene and dihydromyrcene. Their spectra are shown in Fig. 1, and in this and the subsequent figures absorption bands mentioned in the text are accented by a line down the middle in the appropriate spectra.

Geraniolene is considered to be mainly 2 : 6-dimethylhepta-1 : 5-diene,

$$CH_3\cdot CMe{:}CH\cdot CH_2\cdot CH_2\cdot CMe{:}CH_2,$$

although its method of preparation (Bernhauer high-temperature decarboxylation; see Naylor, *loc. cit.*) does not exclude the possibility of considerable amounts of other isomers. Its infra-red spectrum has absorption bands at 1654 and 891 cm.$^{-1}$, and at 1680 and 821 cm.$^{-1}$ which can be ascribed to C=C valence and C—H deformation vibrations respectively of $RR'C{:}CH_2$ and $RR'C{:}CHR''$ groups, in agreement with the above formula (see Table I).

Dihydromyrcene is generally assumed to consist largely of 2 : 6-dimethylocta-2 : 6-diene, $CH_3{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_3$, but its method of preparation (Naylor, *loc. cit.*) suggests that the isomers 2 : 6-dimethylocta-1 : 6-diene, $CH_2{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_3$, and 6-methyl-2-ethylhepta-1 : 5-diene,

$$CH_3{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CEt{:}CH_2,$$

may also be present. Comparison of the spectrum of this material with that of pure 2 : 6-dimethylocta-2 : 6-diene, prepared by an independent method, shows that in addition to the usual bands attributable to the $RR'C{:}CHR''$ groups (at 1678 and 820 cm.$^{-1}$) there are also bands (at 1650 and 889 cm.$^{-1}$) attributable to the $RR'C{:}CH_2$ groups of these alternative isomers. For this reason the dihydromyrcene used in the earlier experiments with hydrogen sulphide and sulphur catalyst was subsequently replaced by the pure 2 : 6-dimethylocta-2 : 6-diene.

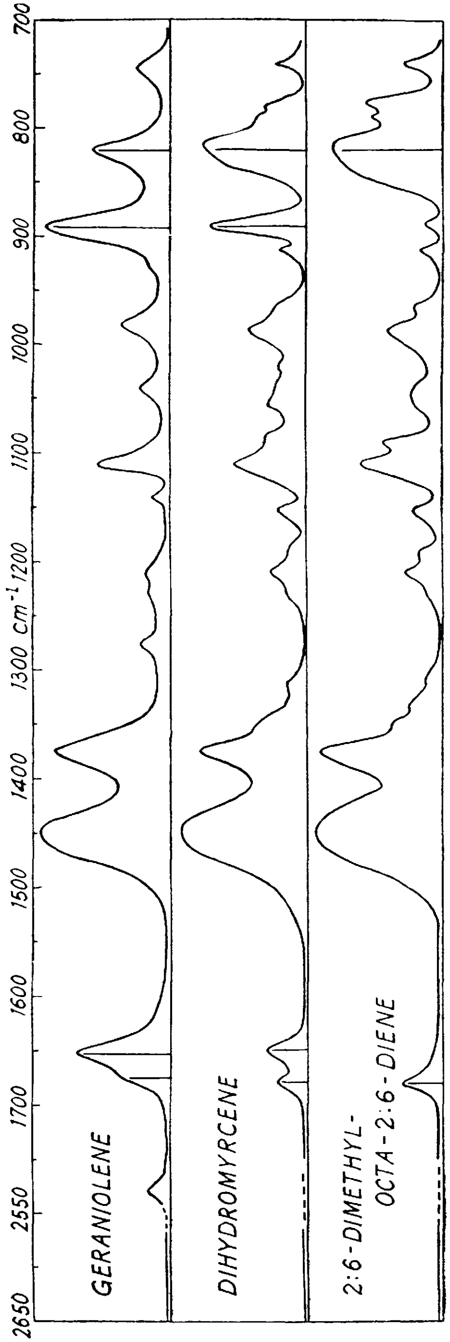
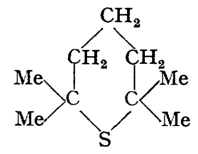
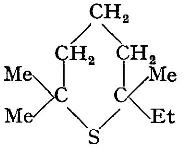


FIG. 1.
Spectra of the hydrocarbons.

Infra-red Analysis of the Reaction Products.—(1) *General.* The chemical aspects of the reactions of geraniolene and dihydromyrcene with hydrogen sulphide have been fully discussed by Naylor (*loc. cit.*). The spectroscopic problem was to investigate certain portions of the products obtained with catalysts that promote " normal " addition according to the Markovnikov rule. In particular we required to establish the presence or absence of 2 : 2 : 6 : 6-tetramethyltetrahydrothiopyran (I) and 2 : 2 : 6-trimethyl-6-ethyltetrahydrothiopyran (II) as reaction products of the respective hydrocarbons.

(I.)




(II.)

We also investigated some products from similar reactions in which the conditions were such that products of " abnormal " addition were to be expected.

The spectra of the reaction products of geraniolene and hydrogen sulphide obtained under conditions of normal addition are given in Fig. 2, the steps in the gradual purification and identification being indicated by the following key: (A) Spectrum of the reaction product, sulphur being used as catalyst. (B) Spectrum of the reaction product, aluminium sulphide being used as catalyst (to avoid the possibility of the catalyst reacting with the hydrocarbon). (C) Spectrum of B after removal of thiols by cupric butyl phthalate. (S) Spectrum of synthetic 2 : 2 : 6 : 6-tetramethyltetrahydrothiopyran.

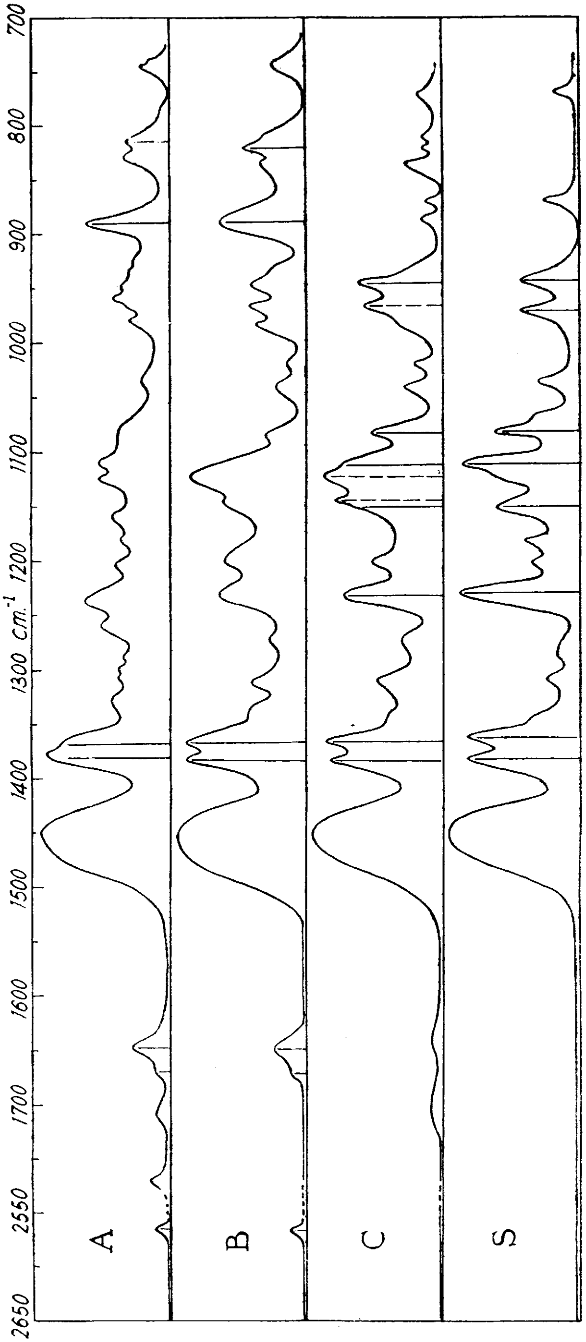


Fig. 2.

Spectra of the "normal" geraniolene-hydrogen sulphide reaction products and of 2 : 2 : 6 : 6-*tetramethyltetrahydrothiopyran* (*Spectrum* S).

The corresponding spectra for the dihydromyrcene reaction are given in Fig. 3, but it should be noted that only (A) refers to the reaction with dihydromyrcene; the remaining spectra are all of products obtained by using the synthetic specimen of the single isomer 2 : 6-dimethylocta-2 : 6-diene of which the spectrum is given in Fig. 1. It should also be noted that (B′) of Fig. 3 is the spectrum of a reaction product obtained under the same conditions as (B) but with some quinol present to remove any peroxides. As in the case of the geraniolene products, (C) and (S) denote respectively the thiol-free product and the independently synthesised cyclic sulphide.

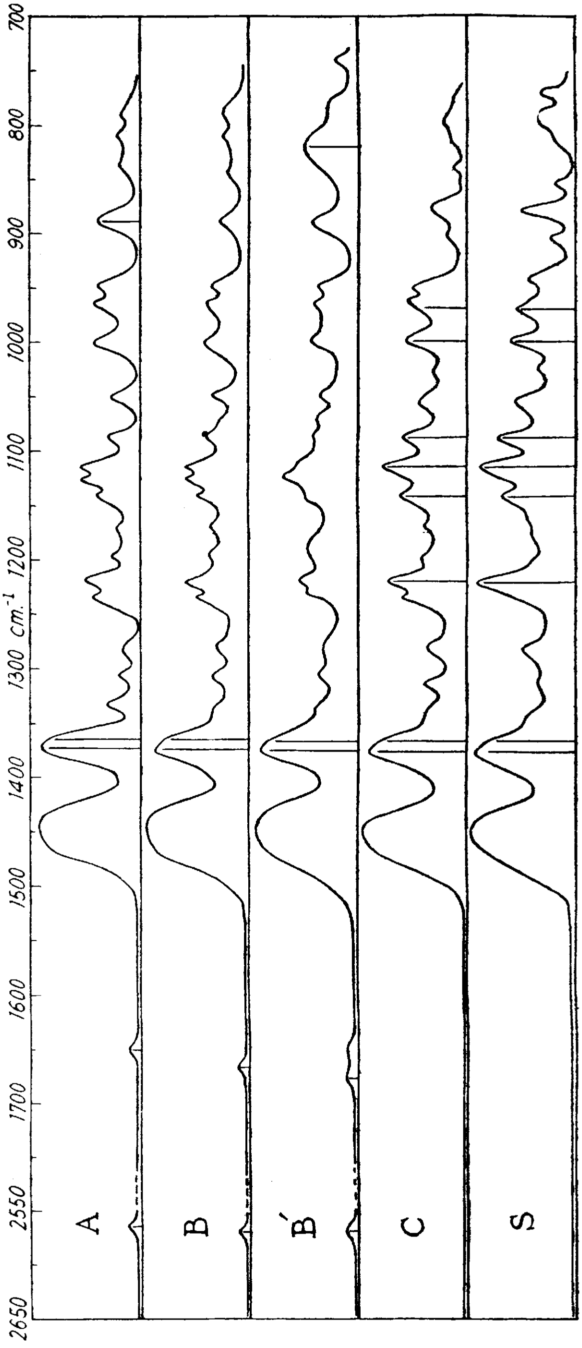


FIG. 3.

Spectra of the "normal" dihydromyrcene–hydrogen sulphide reaction products and of 2 : 2 : 6-*trimethyl*-6-*ethyltetrahydrothiopyran* (*Spectrum S*).

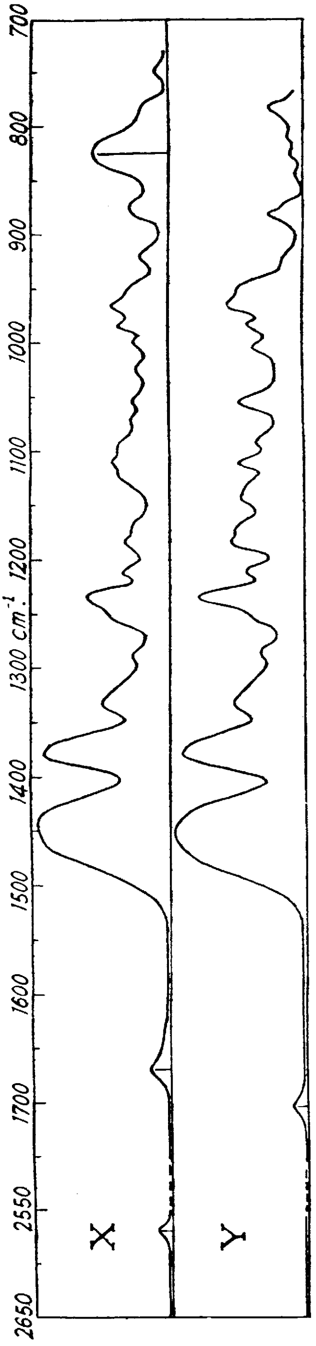


FIG 4.

Spectra of the "abnormal" dihydromyrcene–hydrogen sulphide reaction products.

In Fig. 4 are represented the spectra of the products obtained when 2 : 6-dimethylocta-2 : 6-diene and hydrogen sulphide are irradiated with ultra-violet light—conditions that should promote abnormal addition : (X) is the original unpurified product, and (Y) the thiol-free material.

(2) *The products of the geraniolene–hydrogen sulphide reaction under " normal " conditions* (see Fig. 2). The expected product—2 : 2 : 6 : 6-tetramethyltetrahydrothiopyran—has four methyl groups that occur in pairs, and this should give rise to the splitting of the 1370 cm.$^{-1}$ band. Such a splitting (1381 and 1362 cm.$^{-1}$) is found in the spectrum of the synthetic material (S), and confirms its authenticity. Other bands in the spectrum of (S) which can be used for the identification of this sulphide in the reaction product occur at 1229, 1149, 1111, 1079, 971, and 942 cm.$^{-1}$.

Product A (sulphur as catalyst) has a poorly defined spectrum which shows little splitting of the 1370 cm.$^{-1}$ band, and in addition has absorptions at 1648 and 889 cm.$^{-1}$ characteristic of RR′C⁚CH$_2$ groupings, 1670 and 815 cm.$^{-1}$ characteristic of RR′C⁚CHR″ groupings, and 2570 cm.$^{-1}$ caused by SH groups. In other words, it is obvious that further purification was necessary, and that at least some of the impurities were residual amounts of monothiol.

The aluminium sulphide-catalysed product (B) has a cleaner spectrum—due probably to the absence of any sulphur–geraniolene products—but still retains the other groupings corresponding to the monothiols. However, after removal of these by cupric butyl phthalate (product C) a fairly clean spectrum is obtained with, as required, a pronounced splitting of the 1370 cm.$^{-1}$ band (1381 and 1363 cm.$^{-1}$). In addition, the strong bands which occur at 1231, 1150, 1111, 1082, and 945 cm.$^{-1}$ show that there is a considerable amount of the expected sulphide present. Several well-pronounced bands remain, however, which are not due to the expected product, and one of these obscures the 971 cm.$^{-1}$ position. The three strongest bands which cannot be attributed to this sulphide have their centres at 1144, 1122, and 965 cm.$^{-1}$, all of which are very close to strong absorptions of the synthesised cyclic sulphide.

(3) *The products of the dihydromyrcene–hydrogen sulphide reaction under " normal " conditions* (see Fig. 3). The spectrum of the specially synthesised 2 : 2 : 6-trimethyl-6-ethyltetrahydrothiopyran (S) has absorptions at 1220, 1142, 1116, 1087, 1002, 970 cm.$^{-1}$ which can be used for identification purposes. In this case the splitting of the 1370 cm.$^{-1}$ band is only just detectable, as is to be expected, since there are equal numbers of " paired " and " lone " methyl groups present. It is interesting to note a strong general resemblance between this spectrum and that of 2 : 2 : 6 : 6-tetramethyltetrahydrothiopyran, and this correspondence confirms the closely related structures of these two substances.

Product A (sulphur as catalyst) gives the spectrum shown at the top of Fig. 3. A small proportion of SH groups is indicated by the usual band at 2570 cm.$^{-1}$, and also some unsaturation of the disubstituted type RR′C⁚CH$_2$ by the bands at 1650 and 889 cm.$^{-1}$. The fact that some of the residual unsaturation is of the disubstituted type in this case is surprising in view of the fact that the initial hydrocarbon should have few such groupings. However, product B (with pure 2 : 6-dimethylocta-2 : 6-diene and aluminium sulphide as catalyst) does not show any considerable absorptions in these positions, and the probability that this disubstituted unsaturation is due to some sulphur–dihydromycene reaction products is substantiated by the presence of bands at 1650 and 890 cm.$^{-1}$ in the spectra of such products (unpublished work). Very weak bands at 2570 cm.$^{-1}$ and *ca.* 1660—1670 cm.$^{-1}$ suggest that there is some residue including thiol. Product B′ (obtained as B but with quinol present) has a considerable number of SH and unsaturated groupings—the latter being predominantly of the trisubstituted type (1680 and 820 cm.$^{-1}$). Otherwise its spectrum is very similar to that of B, indicating that the removal of any peroxides that might have been present during the reaction had little effect on the product. This is additional evidence that it is not formed by " abnormal " addition.

Finally, the removal of thiol from (B) by cupric butyl phthalate (product C) caused the disappearance of SH and unsaturation absorptions. The resultant material gives a reasonably clean spectrum. Comparison of this spectrum (C) with that of the synthesised material (S) which was taken with the same path-length of liquid, shows that all the characteristic bands of 2 : 2 : 6-trimethyl-6-ethyltetrahydrothiopyran are present in strength comparable with those of the pure material. One or two weak additional bands are present in (C) which presumably correspond to a small amount of impurity, but the product is very nearly all pure sulphide of the expected type.

(4) *The products of the dihydromyrcene–hydrogen sulphide reaction under " abnormal " conditions* (see Fig. 4). The product (X) was formed by the ultra-violet-catalysed reaction between pure 2 : 6-dimethylocta-2 : 6-diene and hydrogen sulphide and would be expected to be " abnormal " in type. It has a very different spectrum from those products discussed in the preceding section although it does have bands at 2580 cm.$^{-1}$ (SH groups) and at 1670 and 825 cm.$^{-1}$ characteristic of trisubstituted double bands. This means that there is a considerable proportion of monothiol present. Removal of this by the usual method gave product

(Y), which has a spectrum similar to (X) except that the above three bands have disappeared. There remains a weak band near 1700 cm.$^{-1}$ which is probably due to some impurity introduced during the removal of thiol, as such a frequency is characteristic of $C{=}O$ rather than $C{=}C$ groups. The spectrum of this sample is completely different from that of the final " normal " product of Section (3).

Discussion.

We have shown that the spectra of the reaction products under conditions favouring " normal " addition are extremely similar to those of 2 : 2 : 6 : 6-tetramethyl- and 2 : 2 : 6-trimethyl-6-ethyl-tetrahydrothiopyran, but there are certain discrepancies which must be considered before this strong resemblnce can be accepted as conclusive proof of the identities of the reaction products. When spectra differ in this way it may be either because impurities are present, or because the compounds of which the spectra are being compared are really different, but of closely related structure. These two cases, which we shall call (1) and (2), can usually be distinguished. In the former, the main bands of the pure compound should be stronger than the corresponding bands in the unknown for the same cell thickness, unless, of course, a band due to the impurity overlaps one of these " key " bands. From Figs. 2 and 3 it will be seen that this is indeed the case for our comparisons. Again, in case (1) all bands, except the very weakest, detectable in the spectrum of the pure compound should be present in the unknown, whereas in case (2) the number of weak bands may be greater for the pure compound than the unknown. It will be seen that on this criterion also our identification is justified, for although there is one weak band in 2 : 2 : 6 : 6-tetramethyltetrahydrothiopyran (near 1180 cm.$^{-1}$) which does not appear in the (C) spectrum (Fig. 2), this sole exception may well be due to a trace of impurity in the synthetic compound.

In the case of the comparison of the geraniolene product with the synthetic 2 : 2 : 6 : 6-tetramethyltetrahydrothiopyran, it is obvious that the amount of " impurity " is considerable and it is thought that this arises from the presence of other isomers than 2 : 6-dimethylhepta-1 : 5-diene in the original hydrocarbon. The dihydromyrcene product has relatively little impurity, in agreement with the fact that pure 2 : 6-dimethylocta-2 : 6-diene was used for the reaction.

We wish to draw attention in this connection to the power of the infra-red method in detecting by-products in a reaction. The difficulty of sufficiently purifying the product to enable us to use infra-red analysis is a sufficient indication of this, and of the precision of the identification once that purification has been achieved.

Experimental.

The infra-red spectra were taken with the Hilger Double-Beam Spectrometer described by Sutherland and Thompson (*Trans. Faraday Soc.*, 1945, **41**, 174). They were recorded under double-beam conditions so that the absorption of radiation by water vapour in the atmosphere did not interfere with the spectra.

Table II.

Analytical data for the samples investigated spectroscopically.

Compound.	B. p.	Refractive index.	Found, %. C.	Found, %. H.	Found, %. S.	Calculated, %. C.	Calculated, %. H.	Calculated, %. S.
Geraniolene	36°/10 mm.	$n_D^{18°}$ 1·4408	87·0	12·9	—	87·1	12·9	—
Dihydromyrcene...............	60 /16 mm.	$n_D^{17°}$ 1·4542	87·2	12·9	—	87·0	13·0	—
2 : 6-Dimethylocta-2 : 6-diene	56 /14 mm.	$n_D^{17°}$ 1·4517	87·0	13·2	—	87·0	13·0	—
Geraniolene products A ...	86—87 /16 mm.	$n_D^{18°}$ 1·4812	68·2	11·4	20·2	68·4	11·4	20·2
,, ,, B ...	69—71 /11 mm.	$n_D^{18°}$ 1·4729	68·5	11·2	19·9	,,	,,	,,
,, ,, C ...	66 /11 mm.	$n_D^{18°}$ 1·4732	68·2	11·3	19·9	,,	,,	,,
,, ,, S ...	66 /12 mm.	$n_D^{19°}$ 1·4763	68·3	11·6	20·1	,,	,,	,,
" Normal " dihydromyrcene products A	83 /9 mm.	$n_D^{17°}$ 1·4858	69·9	11·4	18·6	69·8	11·6	18·6
,, B	87—88 /9 mm.	$n_D^{16°}$ 1·4798	69·6	11·6	18·6	,,	,,	,,
,, B′	86—88 /10 mm.	$n_D^{20°}$ 1·4782	69·7	11·5	18·7	,,	,,	,,
,, C	84 /10 mm.	$n_D^{20°}$ 1·4792	69·4	11·5	18·3	,,	,,	,,
,, S	87 /13 mm.	$n_D^{20°}$ 1·4849	69·6	11·7	18·6	,,	,,	,,
" Abnormal " dihydromyrcene products X............	92 /11 mm.	$n_D^{19.5}$ 1·4767	69·8	11·6	18·6	69·8	11·6	18·6
,, Y	46 /1 mm.	$n_D^{15°}$ 1·4831	69·7	11·5	18·2	,,	,,	,,

A rock-salt prism was used throughout for this work, and the effective slit-widths (in cm.$^{-1}$) were 40 at 2000 cm.$^{-1}$, 12 at 1600 cm.$^{-1}$, 6 at 1000 cm.$^{-1}$, and 5 at 700 cm.$^{-1}$. The positions of the bands are accurate to 2 cm.$^{-1}$ up to 1300 cm.$^{-1}$, 4 cm.$^{-1}$ from 1300 to 1900 cm.$^{-1}$, and 20 cm.$^{-1}$ at any higher frequencies in this work.

The experimental details of the olefin–hydrogen sulphide reactions have been given by Naylor (*loc. cit.*) and it will suffice here to give the physical properties and analytical figures for the samples investigated. These figures were obtained by Naylor at Welwyn, and the samples were then sealed in nitrogen and transmitted to Cambridge. The spectra were taken in a rock-salt cell of 0·06 mm. thickness, immediately after the samples had been unsealed.

Our thanks are due to Drs. E. H. Farmer and R. F. Naylor, of the British Rubber Producers' Research Association, for bringing this problem to our notice, and for providing us with all the specimens investigated. We are also grateful to them for much helpful discussion during the course of the work.

One of us (N. S.) is indebted to St. Catharine's College, and the Dunlop Rubber Co. Ltd., for financial help during this investigation. The spectrometer used was provided by a joint grant from the Royal Society and Imperial Chemical Industries Ltd.

LABORATORY OF COLLOID SCIENCE, CAMBRIDGE.

[*Received, February 6th,* 1947.]