however, that each isomer has been prepared in a directed manner from a compound of definite and different polarity and that each adds a polar compound in a directed manner corresponding to the method of preparation for each seems to indicate that the two isomers are electronic rather than geometrical. Moreover, the fact that the 2-pentene prepared from 3-bromopentane is transformed into a more stable form is in accord with this theory.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE]

ISOMERS OF 2-PENTANE. III. THE ULTRAVIOLET ABSORPTION SPECTRA OF THE ISOMERIC 2-PENTENES[1]

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A study of the ultraviolet absorption spectra of the isomeric 2-pentenes prepared by M. L. Sherrill and co-workers of this Laboratory[2] has been of particular interest in its relation to the electro-isomerism of these compounds and has given further experimental evidence in support of Kharasch's theory of the partial polarity of the ethylene bond.[3] The effect of unsaturation on all of the optical properties of a compound is well known but this effect is particularly marked in the ultraviolet absorption spectra. For example, a 3-cm. length of optically pure hexane transmits to λ = 2000 Å. or even further, while the limit of transmission for the same length of pentene is in the region of λ = 2600–2800 Å. A quantitative study of the influence of the ethylene group on the infra-red and ultraviolet absorption has been made by Henri,[4] and he shows that, in general, the simple ethylenic compounds have two bands in the ultraviolet, one of very small intensity in the region 2600–2300 Å. and another very intense band in the extreme ultraviolet, λ = 2000–1800 Å. These conclusions were based on the investigation of several olefin acids and of allyl alcohol, the *exact* position of the bands due to the double bond being dependent upon the other groups in the molecules. The results of recent spectrographic study of substances in liquid, solution or vapor phase point to the conclusion that ultraviolet absorption is closely related to *electronic* motion within the molecule and on this basis one would expect that slight differences in the electronic condition of the molecule might be detected by light absorption methods.

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[1] Presented in abstract before the Organic Division at the Swampscott Meeting of the American Chemical Society, September, 1928.

[2] (a) Sherrill, Otto and Pickett, THIS JOURNAL, **51,** 3023 (1929); (b) Sherrill, Baldwin and Haas, *ibid.*, **51,** 3034 (1929).

[3] M. S. Kharasch and F. R. Darkis, *Chem. Reviews*, **5,** 571 (1928).

[4] V. Henri, "Études de Photochemie," Gauthier-Villars, Paris, **1919,** p. 98.

The determination of the absorption curves for the isomeric 2-pentenes offered a promising point of attack in the study of electro-isomerism and this investigation was undertaken at the suggestion of Dr. M. S. Kharasch. Since traces of impurities have such a profound effect upon the absorption spectra, the problem resolved itself into the preparation of these isomers in a high degree of purity and it has been only by the constant comparison and checking of absorption measurements with the physical and chemical properties as determined by Sherrill and collaborators[2] that it has been possible to obtain what seems to be confirmatory evidence of the correctness of Kharasch's theory of the electro-isomerism of the 2-pentenes.

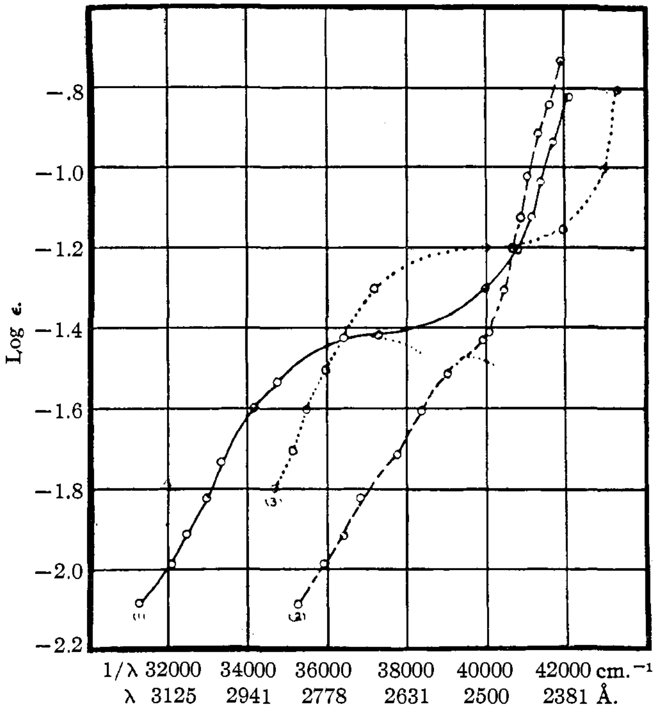

Fig. 1.—(1) ——, 2-Pentene prepared from 2-bromopentane, n_D^{20} 1.37849; (2) – – –, 2-pentene prepared from 3-bromopentane, n_D^{20} 1.37945; (3) ...., trimethylethylene according to Lüthy [*Z. physik. Chem.*, **107**, 285 (1923)].

Our results show that the absorption curve for the 2-pentene prepared from 3-bromopentane differs markedly from that of the 2-pentene obtained from 2-bromopentane (Fig. 1). The absorption curves of these two isomers are so characteristic that they have given a most delicate method of identifying these isomers as well as of differentiating them from 1-pentene and the polymeric forms of 2-pentene which may be present as impurities. The absorption spectrum of trimethylethylene has been measured by Lüthy[5] and that part of the curve in the region in which the 2-pentenes were examined has been reproduced in Fig. 1. A marked "step-out" in the general absorption of a substance indicates an absorption band of such small persistence that the complete band is not evident and such a step-out is shown by all of the pentenes in the region λ 2700–2500 Å.

The curves for the stable 2-pentene (Curve 1, Fig. 1) and trimethylethylene (Curve 2, Fig. 1) are almost exactly similar in form and differ only in the position of the band and to a slight degree in intensity,[6] whereas the curve for the isomeric 2-pentene prepared from 3-bromopentane is very different. The broad step-out has disappeared entirely and there is only the slightest tendency toward an absorption band. In the longer wave lengths this isomer transmits farther; in the shorter wave lengths slightly less. The differences are striking and of great interest in connection with the possibility of the electro-isomerism of the 2-pentenes. The shallow absorption band in this region is characteristic of all ethylenic compounds and if this absorption band is related to the second pair of electrons, the so-called labile pair, in the double bond it would be in this band that one would expect differences in the absorption of electronic isomers to be most evident and there should be little or no difference in the second band in the far ultraviolet. In this connection it is of interest to note that in seven pairs of *cis-trans* isomers which have been examined by quantitative methods[7] the two forms have very similar absorption curves but the *trans* form is somewhat more absorptive and this difference becomes *much more marked* the shorter the wave length. It would seem, therefore, that with geometrical isomerism it is the intense band in the far ultraviolet which differs with the two isomers while in electro-isomerism it is the band of low intensity in the near ultraviolet which shows the marked differences. Although experimental data are too meager to justify far-reaching conclusions, these results certainly suggest the possibility that the absorption band in the far ultraviolet is related to the characteristic frequency of the stable pair of electrons in the double bond and these electrons are primarily concerned in *cis-trans* isomerism, while the second pair of electrons, being much more labile, produce the shallow band of much lower frequency and, according to the theory of Kharasch, it is the relative position of this pair of electrons which determines electronic isomerism.[3]

[5] Lüthy, *Z. physik. Chem.*, **107**, 285 (1923).

[6] Repetition of the work on trimethylethylene in this Laboratory corroborates Lüthy's measurements as to the position of the band but shows the step-out at log $\epsilon = -1.4$ instead of -1.2.

[7] Errera and Henri, *Compt. rend.*, **181**, 548 (1925).

The absorption curves for different preparations of 2-pentene prepared from 3-bromopentane by the action of alcoholic potassium hydroxide and from 3-pentanol by the action of 60% sulfuric acid are given in Fig. 2. The solid line curve gives results for three completely independent preparations of 2-pentene made from different samples of synthetic 3-bromopentane. The broken line curves show the absorption of 2-pentene prepared from synthetic 3-bromopentane which, from its index of refraction, contained some 2-bromopentane. Where the index of refraction shows a mixture of 2- and 3-bromopentane the absorption curve of the pentene prepared from the mixture indicates at once that the product is a mixture of the two isomeric 2-pentenes, (Curves 2 and 2′, Fig. 2) and calculations of the relative amounts of the two isomers on the basis of the extinction coefficient as a linear function of the concentration, give very satisfactory agreement with those calculated from the index of refraction of the mixture. The fact that these results are in agreement also with those obtained from the addition of hydrogen bromide to the pentene

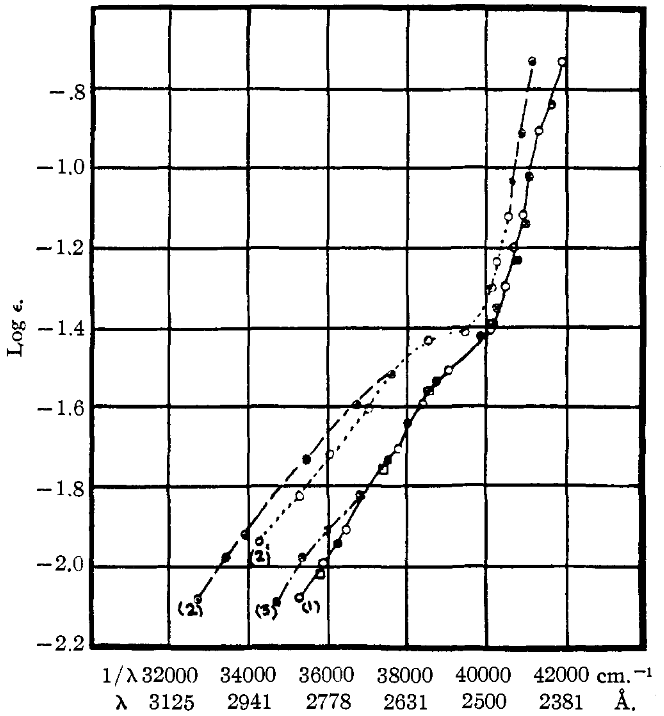

Fig. 2.—Different preparations of 2-pentene. (1) From 3-bromopentane, ○, n_D^{20} 1.37945; ● n_D^{20} 1.37965; □ n_D^{20} 1.37965. (2) From 3-bromopentane, ⊙ n_D^{20} 1.37923; ○. . . ., n_D^{20} 1.37909. (3) From 3-pentanol (synthetic), ⊗, n_D^{20} 1.37935.

and analysis of the mixture of bromopentanes has established confidence in the accuracy of our conclusions. In all preparations of 2-pentene which were made directly from the alcohol there is a small amount of a more absorptive material which is evidenced by a slightly increased absorption in the longer wave lengths. Inasmuch as sulfuric acid increases the polymerization of the olefins and the higher-boiling fractions contain a greatly increased amount of this more absorptive material and have a correspondingly higher index of refraction, the increased absorption is no doubt due to the presence of polymeric forms of the pentene. The delicacy of the spectrographic method of examination is shown in Fig. 3, where a difference in boiling point of three-tenths of a degree in the azeotropic mixtures gives an enormous difference in absorption, although the increase in index of refraction is comparatively slight. No such striking increase in the absorption of the higher fractions of 2-pentene obtained from the bromopentanes was found since the tendency to polymerize is very much less when prepared by alcoholic potash than by the action of sulfuric acid.

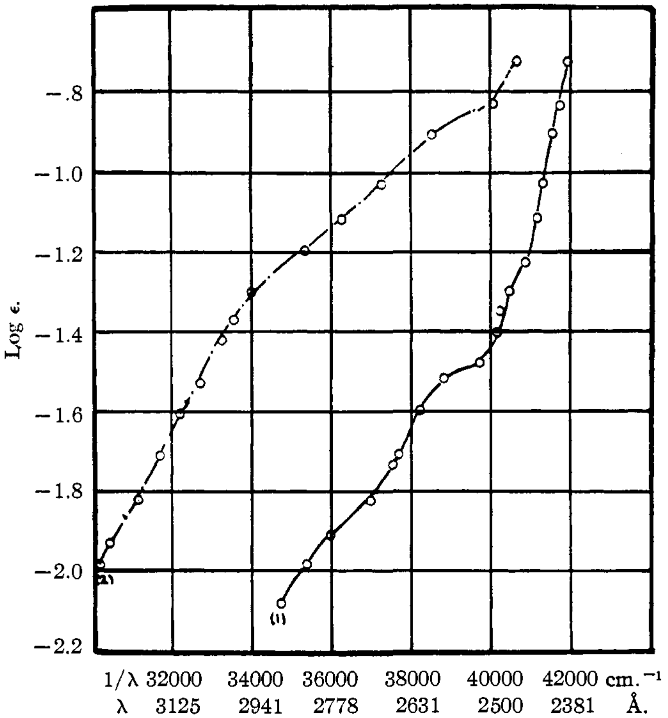

Fig. 3.—Fraction of 2-pentene from 3-pentanol. (1) Azeotropic mixt. with CH_3OH, b. p. 30.9–31.1°; C_5H_{10} n^{20}_D 1.37935. (2) Azeotropic mixt. with CH_3OH, b. p. 31.1–31.5°; C_5H_{10} n^{20}_D 1.37988.

In the preparation of the 2-pentene from 2-bromopentane and 2-pentanol, small amounts of 1-pentane are formed and by means of absorption spectra measurements it was possible to follow the separation of these isomers. Figure 4 shows the absorption curves of the different fractions in the distillation of a methyl alcohol solution of 2-pentene prepared from 2-bromopentane. Results from bromination and hydrobromination data[2b] showed that the low-boiling fraction contained the 1-pentene, and the absorption curve for the fraction (Curve 1) shows greater transmission than either of the 2-pentenes.[8]

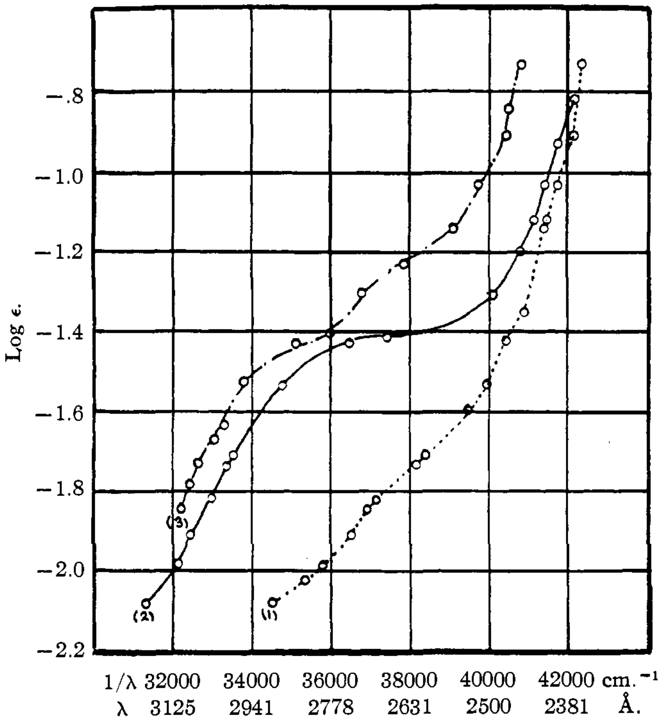

Fig. 4.—Fractionation of 2-pentene prepared from 2-bromopentane. (1) Azeotropic mixt. with CH_3OH, b. p. 29.9–30.1°; C_5H_{10} n^{20}_D 1.37680. (2) Azeotropic mixt. with CH_3OH, b. p. 30.75–30.95°; C_5H_{10}, n^{20}_D 1.37849. (3) Azeotropic mixt. with CH_3OH, b. p. 30.95–31.5°; C_5H_{10}, n^{20}_D 1.37876.

The effect of diffused light on the absorption spectrum of the 2-pentene prepared from 3-bromopentane is shown in Fig. 5. The solid line (Curve

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[8] A recent preparation in this Laboratory of 1-pentene confirms the low boiling point and index of refraction, but the 1-pentene contains traces of allyl bromide from which it was prepared. This impurity increases the absorption tremendously but even so the preparation transmits further than either of the 2-pentenes, thus confirming our conclusion that the low-boiling fraction is 1-pentene.

1) gives the absorption of the original material and the broken line (Curve 2) that of the same material after standing in a sealed glass tube and exposed to the diffused sunlight of the laboratory for three months. In comparison with the absorption curve of the 2-pentene from 2-bromopentane (Curve 3), which according to Kharasch should be the stable form, this light-transformed material shows the presence of a more absorptive material of higher index of refraction. The most probable conclusion, and one which is in accord with results of hydrobrominating this substance, is that this curve represents a mixture of the isomeric 2-pentene together with a small amount of the very absorptive polymer.

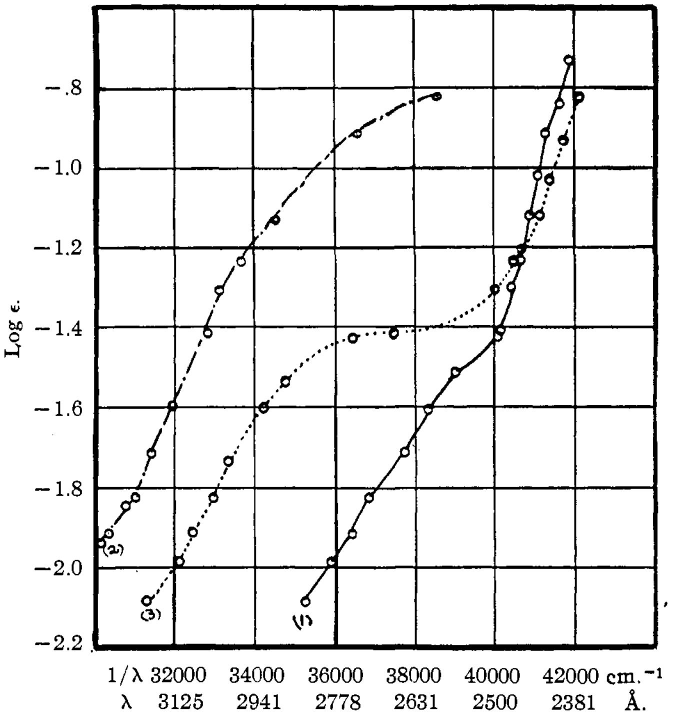
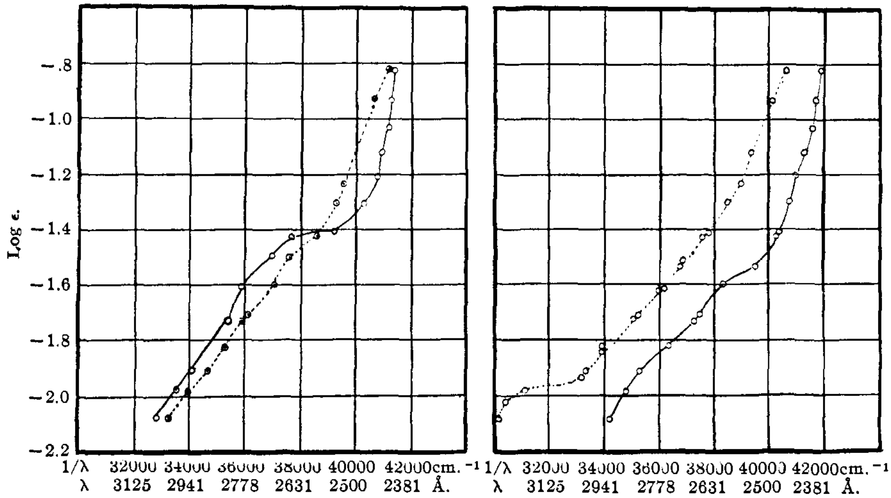


Fig. 5.—(1) ——, 2-Pentene prepared from 3-bromopentane, n_D^{20} 1.37965; (2) —·—, 2-pentene after 3 months in sunlight and diffused light, n_D^{20} 1.37934; (3)......., 2-pentene prepared from 2-bromopentane, n_D^{20} 1.37849.

The study of the absorption curves of the two isomeric pentenes before and after exposure to ultraviolet light from the mercury arc for eight and a half hours shows an opposite effect of light on the two isomers (Fig. 6). The 2-pentene prepared from 2-pentanol shows much greater stability and the absorption is shifted only very slightly toward the ultraviolet, whereas the absorption of the 2-pentene from 3-bromopentane is shifted toward the visible and a new band in the region of λ = 3125 Å. indicates a decomposition with the formation of a new substance.

The study of the progressive action of light on these isomers is being continued in this Laboratory and the results so far obtained give strong support to our conclusion that the two isomers are electromers. Their relative stabilities are in accord with the postulates of Kharasch's theory and are not in agreement with predictions based on the behavior of *cis-trans* isomers. The usual action of light on geometrical isomers is to transform the more absorptive *trans*-form into the less absorptive *cis-form*, whereas with the isomeric 2-pentenes the more absorptive isomer is the stable form.

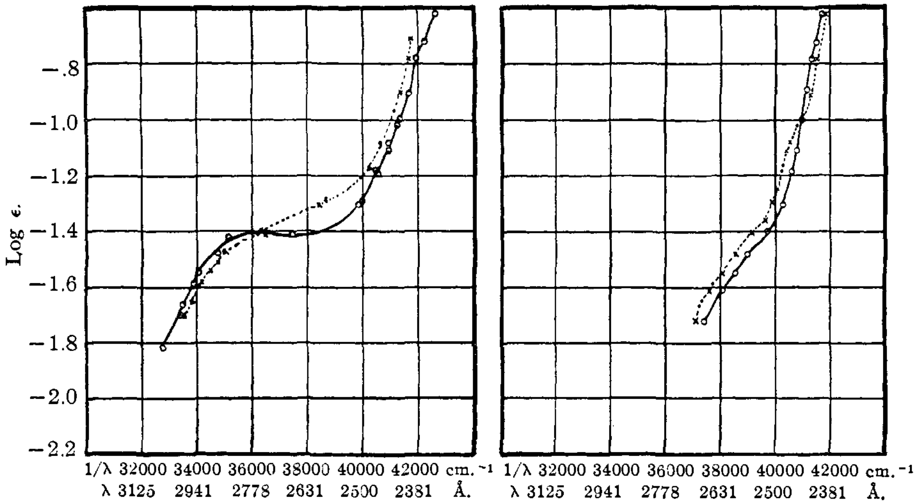


——, 2-Pentene prepared from 2-pentanol, n^{20}_{D} 1.37968; - - - -, 2-pentene after exposure to ultraviolet light for 8.5 hours, n^{20}_{D} 1.37989.

——, 2-Pentene from 3-bromopentane, n^{20}_{D} 1.37930; - - - -, 2-pentene after exposure to ultraviolet light for 8.5 hours, n^{20}_{D} 1.37956.

Fig. 6.—Action of ultraviolet light on the 2-pentenes.

Inasmuch as the relative amounts of 3-bromopentane and 2-bromopentane obtained by hydrogen bromide addition to the 2-pentenes are dependent upon the solvent used, it is of interest to compare the absorption spectra of each of the 2-pentenes when photographed in a non-polar solvent such as hexane and in a polar solvent, glacial acetic acid. V. Henri and his collaborators, in a long series of investigations of the ultraviolet absorption spectra of organic substances in vapor phase and in various solvents, have shown that the absorption curve in hexane solution most closely resembles that in the vapor phase and have regarded the absorption curve in hexane as the "normal" spectrum. Our results show a very slight shift in intensity between the curves of the pure liquid pentene and its hexane solution, due no doubt to the difficulty in determining the exact concentration of the solution of the very volatile 2-pentene. In order to study the absorption spectrum in the region of the "step-out" it was necessary to use very concentrated solutions, as the intensity of this band is too small to measure in dilute solution. Solutions of each isomer in hexane and in glacial acetic acid were made up in the ratio of three volumes of pentene to one volume of solvent and the molar concentration was calculated from the density determinations. The absorption curves for these solutions are given in Fig. 7. With each isomer the curve for the hexane solution coincides practically with that obtained from the examination of the liquid pentene, but in glacial acetic acid the curve for the 2-pentene which had been prepared from 2-bromopentane is shifted slightly toward that of the isomeric 2-pentene and that of the second isomer prepared from 3-bromopentane is shifted toward the curve for the first isomer. These results in acetic acid solution are surprising in that they involve, in the curve for one isomer, a shift of absorption toward the ultraviolet end of the spectrum in the longer wave lengths and toward the visible in the shorter wave lengths. With the other isomer the shift in absorption is exactly opposite and these results are in complete agreement with predictions based on hydrogen bromide addition to the two isomers.[2] When hydrogen bromide gas is added to the 2-pentene prepared from 2-bromopentane either without any solvent or in a non-polar



2-Pentene prepared from 2-bromopentane; ——, 2-pentene dissolved in hexane; ...., 2-pentene dissolved in glacial acetic acid.

2-Pentene prepared from 3-bromopentane; ——, 2-pentene dissolved in hexane; ...., 2-pentene dissolved in glacial acetic acid.

Fig. 7.

solvent the product is 98–100% 2-bromopentane; with the other isomer the product is 98–100% 3-bromopentane.

The absorption curves in hexane give no evidence of any change in electronic condition brought about by the solvent and on this basis, if the isomers are electronic, addition of hydrogen bromide in a non-polar solvent would give 100% 2-bromopentane or 100% 3-bromopentane, as the case might be. Further, if the isomers are electronic a polar solvent such as glacial acetic acid would give a different electrical environment with a consequent effect on the relative position of the pair of labile electrons and therefore of the polarity of the double bond. In the addition of hydrogen bromide this electronic shift would be indicated by a change in the relative amounts of 2-bromo- and 3-bromopentane obtained; addition of hydrogen bromide to the 2-pentene obtained from 3-bromopentane when the pentene is dissolved in glacial acetic acid gives 78% of 3-bromopentane and 28% of 2-bromopentane; addition to the other isomer of 2-pentene in glacial acetic acid gives 85% of 2-bromopentane and 15% of 3-bromopentane. In ultraviolet absorption the effect of the polar solvent should be most evident in the region of the spectrum where the absorption is directly related to the characteristic frequency of the pair of labile electrons. Our spectrographic results so far all point to the conclusion that the band at λ2500–2700 Å. is due to the electronic motion of the second or labile pair of electrons in the double bond and it is exactly here that the pronounced changes in the absorption curves of the acetic acid solutions are shown.

Although no one piece of evidence is completely conclusive in itself in establishing the electro-isomerism of the 2-pentenes, the complete agreement of results based on methods of preparation, directive addition of hydrogen bromide and ultraviolet absorption spectra make such a conclusion the most reasonable interpretation. The differences in physical properties of the two isomers, although slight, certainly indicate two distinct substances. Kharasch and Darkis[3] have pointed out that there are no experimental data which would justify the assumption that *cis-trans* isomers add an unsymmetrical reagent in a different manner and base their conclusions on the electro-isomerism of the 2-pentenes before and after exposure to light on the change in the directive addition of hydrogen bromide. Independent confirmation of their theory is obtained in the preparation by Sherrill and collaborators in this Laboratory of two isomeric 2-pentenes from either 3-bromopentane or 3-pentanol and from 2-bromopentane. Since these preparations were from substances which differed primarily in their electronic structure due to the difference in position of the electronegative bromine atom, or hydroxyl group, it is reasonable to expect that the pentenes formed would differ in electronic structure, but there is no reason to predict or expect a different spatial configuration as in geometrical isomerism.

In the spectrographic study of geometrical isomers the *trans* form, which is the less stable in light, is more absorptive than the *cis* form. In the 2-pentenes the isomer which is less stable in light is the less absorptive. *Cis-trans* isomers show their marked differences in absorption in the far ultraviolet; the 2-pentenes show their marked differences in the near ultraviolet. In the study of the 2-pentenes there has been no experimental result which is not readily explained on the basis of electronic isomerism, whereas a number of results cannot be reconciled with the previously established behavior of geometrical isomers.

Experimental

The absorption spectra measurements were made by means of a Hilger quartz spectrograph (E2) using an iron spark as a source of light. The sparking apparatus consisted of a 0.25 kilowatt transformer and condenser of approximately 0.03 m. f. capacity as recommended by Hilger for spectrum work. The rectangular iron electrodes, cross-section 2 mm. by 3 mm., were carried in a holder with vertical and horizontal adjustment and the width of the spark-gap was kept at 2 mm. Measurements of the absorption were made in small Baly absorption tubes of clear fused quartz with optically worked ends fused to the tube and with ground quartz connections such that the length of absorbing liquid could be adjusted without the use of the ordinary rubber connections. This avoidance of rubber and also of cement for fastening the quartz plates to the tube was of great advantage in maintaining the purity of the liquids under examination. The length of the absorbing medium was varied from 70 mm. to 4 mm. Lumière and Jougla photographic plates were used throughout the investigation. The extinction coefficients were determined by the photographic method of comparison spectra developed by Henri.[9]

The intensity of the incident light was varied by varying the time of exposure and a uniform time of ten seconds was adopted for photographing the spectrum of the solvent. Between each two spectra of the solution exposed for forty seconds and sixty seconds, respectively, was photographed the spectrum of the solvent through the same thickness, for ten seconds. The duration of the exposure was carefully timed and for the times which were used the validity of Schwarzschild's law has been accurately established

$$\frac{I_0}{I} = \left(\frac{t}{t_0}\right)^n$$

where I_0 is the intensity of the incident light; I, the intensity of the transmitted light; t_0 is the time of exposure through the solvent of a given thickness; t, the exposure time through the solution of the same thickness, and n, a constant dependent on the photographic plates used. The

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[9] Ref. 4, p. 5.

value of this constant was checked in this Laboratory by comparison with the absorption curve of potassium chromate in 0.05 N potassium hydroxide.[10] Extinction coefficients for this curve were determined both by photoelectric and different photographic methods and the close agreement of our results checked not only the value of the constant for the photographic plates but gave a very satisfactory check on the accuracy of our experimental procedure.

A Leitz binocular was used for determining the points of equal density between the spectra of solution and solvent of the same thickness and the wave lengths were identified from the known wave lengths of the iron spark. By combining Schwarzchild's law with the Bunsen-Roscoe law, which defines the extinction coefficient, $\epsilon = 1/cd \log I_0/I$, and substituting the value of $n = 0.9$, the extinction coefficients can be calculated from the experimental data by the following formula

$$\epsilon = \frac{0.9}{cd} \log \frac{t}{t_0}$$

where c is the concentration in moles per liter, d is the thickness in cm., t is the exposure time for solution, and t_0 for solvent.

Where the absorption spectrum of the pure liquid pentene was photographed, the molar concentration was calculated from the density and as a comparison spectrum the spark through the same thickness of optically pure hexane was used rather than the spark alone, since the density of hexane (0.660) is close to that of the pentene (0.650). In determining the effect of solvent on the absorption spectra of the 2-pentene, very concentrated solutions were used for two reasons: first, such concentrated solutions are necessary in order to obtain the region in which the band of low intensity is found; second, glacial acetic acid is itself quite absorptive and solutions containing too large proportions of the acid would not transmit sufficiently far to study the region in which this shallow band appears. Two cc. of solvent was added to 6 cc. of pentene and the molar concentration was calculated from the density. A solution of 2 cc. of glacial acetic acid in 6 cc. of hexane was used for the comparison spectrum with the acetic acid solutions of the 2-pentenes.

The optical purity of the solvent in spectrographic work is of the greatest importance and methods of purification of organic solvents have been worked out in Henri's laboratory.[11] One liter of hexane from petroleum (b. p. 65–70°) was shaken for twelve hours with 150 cc. of fuming sulfuric acid (10%), the hexane was decanted and this process was repeated twice with fresh amounts of fuming sulfuric acid. It was then shaken for twelve hours with 150 cc. of concentrated sulfuric acid (sp. gr. 1.84), washed twice with distilled water and shaken for another twelve hours each with (1) 150 cc. of 10% sodium carbonate solution, (2) 150 cc. of a mixture containing 100 cc. of normal potassium permanganate and 50 cc. of 10% sodium carbonate and (3) 150 cc. of a mixture containing 50 cc. of 10% sulfuric acid and 100 cc. of normal potassium permanganate. The hexane was then decanted, washed several times with water,

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[10] Weigert, "Optische Methoden der Chemie," Akademische Verlagsgesellschaft, Leipzig, **1927**, p. 236; Röszler, *Ber.*, **59**, 2608 (1926); Scheibe, May and Fischer, *ibid.*, **51**, 1332 (1924).

[11] Castille and Henri, *Bull. soc. chim. biol.*, **6**, 299 (1924); A. Lüthy, ref. 5; Weigert, ref. 10, p. 212.

dried over sodium wire and distilled with a fractionating column. The hexane thus prepared transmitted the copper line λ 2105 Å., which is the limit of transmission of this type of spectrograph. The glacial acetic acid was purified by repeated recrystallization of the C. P. glacial acetic acid obtained from the General Chemical Company. The 2-pentenes were thoroughly dried over fused calcium chloride before spectrographic examination.

Summary

The ultraviolet absorption spectra of the 2-pentene prepared from 3-bromopentane or 3-pentanol and of the 2-pentene from 2-bromopentane or 2-pentanol show marked differences, particularly in the region of the shallow absorption band in the near ultraviolet. The absorption curves of the two isomers are so characteristic that they have given an excellent method of identifying these isomers as well as of differentiating them from 1-pentene and the polymeric forms of 2-pentene which may be present as impurities.

The effect of a polar solvent, glacial acetic acid, as compared with the non-polar solvent, hexane, on the absorption spectra of the two isomeric 2-pentenes shows that the acetic acid in each case shifts the absorption slightly toward that of the other isomer, while in hexane solution each curve is almost identical with that for the corresponding pure liquid pentene. These results are in accord with the addition reactions of the isomeric pentenes in the two solvents and indicate the existence of electronic isomers. In a non-polar solvent each isomer retains its identity; in a polar solvent there is an electronic shift with the consequent formation of some of the other isomer.

Absorption spectra measurements of the 2-pentene from 3-bromopentane before and after prolonged exposure to diffused light show a shift in the absorption corresponding to a transformation into the isomeric 2-pentene, together with the formation of some more absorptive polymer. When exposed to the ultraviolet light from the mercury arc for eight to nine hours, the absorption spectrum of 2-pentene obtained from 3-bromopentane or 3-pentanol shows a decided shift of the absorption toward the visible, while the isomeric 2-pentene from 2-bromopentane or 2-pentanol under identical conditions is quite stable and shows only a very slight shift of absorption in the opposite direction, that is, toward the absorption curve of the isomeric 2-pentene.

The results of the spectrographic examinations of the isomeric 2-pentenes are in accord with the interpretation of electronic isomerism as proposed by Kharasch, but are not in agreement with the previously established behavior of geometrical isomers.

South Hadley, Massachusetts