tion in each case had slightly higher values, $d^{20}_4$ 0.6535, $n^{20}_{\mathrm{D}}$ 1.3813. These data indicate at least 55–60% of the *cis* form and the absorption spectra measurements showed a similar excess of the *cis* over the *trans* form.

### Pentene-2 from 3-Pentanol

**Pentanol-3.**—Pentanol-3 (b. p. 115.65 ± 0.05° at 760 mm., $d^{20}_4$ 0.8219, $n^{20}_{\mathrm{D}}$ 1.4097) was synthesized from ethyl formate and ethylmagnesium bromide.

**Pentene-2 (75% *trans* Form).**—Pentene-2 (84% yield, 2285 g.) was obtained from 3-pentanol by the action of 9 molar sulfuric acid.[1,20] The azeotropic mixture boiled at 31.4 ± 0.20° at 760 mm. The pentene-2 was distilled twice through the Fenske column B. A small amount (5.2%) distilled from 31.2 to 36.5°, the remainder at 36.25 ± 0.10°. The refractive index and density (Table I) of all fractions of the latter were practically identical and are those obtained previously for pentene-2 by most investigators. The physical data indicate that this contains about 75% of the *trans* form and the ultraviolet absorption spectrum showed that this form predominated.

## Summary

Each of the geometrical isomers of pentene-2 has been prepared by a method which should give only one isomer. The boiling points, refractive indices and densities have been determined; the *cis* form has the higher values for these constants. The assignment of structure based on the synthesis is in accord with that determined by absorption spectra measurements.

The approximate proportion of the two isomers of pentene-2 prepared by four other methods has been determined by a comparison of these physical constants.

SOUTH HADLEY, MASS. RECEIVED AUGUST 11, 1937

---

[20] Norris, *et al.*, THIS JOURNAL, **49**, 885 (1927); "Organic Syntheses," John Wiley and Sons, Inc., New York, 1927, Vol. VII, p. 76.

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE]

# The Ultraviolet Absorption Spectra of the Isomers of Butene-2 and Pentene-2

BY EMMA P. CARR AND HILDEGARD STÜCKLEN

On the basis of electron diffraction measurements of the two isomers of butene-2,[1] the higher boiling isomer was identified as the *cis* form. This assignment was in accord with the molecular configuration which had been deduced by Lucas and collaborators[2] from chemical evidence and is in agreement with that given by Kistiakowsky and collaborators[3] which was based in part on the fact that the heat of hydrogenation of the high boiling butene-2 was identical with that for cyclohexene. Further confirmation for this assignment has been obtained in this Laboratory from measurements of the ultraviolet absorption spectra of the two butenes and cyclohexene in vapor phase in the Schumann region.

The study of the absorption spectra of a number of simple olefin hydrocarbons[4] in the region between $\lambda$ = 2400 and 1600 Å. has shown that the position of the first absorption band in each compound is determined primarily by the number of hydrogen atoms bound to the carbon atoms of the double bond and is practically independent of the nature of the alkyl substituents. The relationship is applicable also to the cyclic hydrocarbons, as our measurements of benzene and diphenyl showed. The recent study of the absorption spectrum of cyclohexene gives another illustration of this same relationship.

It seems definitely established that this first band or in many compounds the first few bands, which are found in the region between 2300 and 1900 Å. may be ascribed to an electronic excitation which is characteristic of the $\mathrm{C{=}C}$ linkage. In general, the spectra of the seventeen aliphatic hydrocarbons which have been measured in that region show only diffuse bands; it is only in the case of *cis* and *trans* butene-2 that the single vibrations are resolved in this group of bands. The very marked difference in the fine structure of the bands, together with slight shifts in position and very different intensity relationships has given new evidence which confirms the earlier assignments of molecular configurations to the isomers of butene-2 and also gives a basis for the identification of the isomers of pentene-2.

Comparison of the absorption spectra curves of the isomers of butene-2 with that of cyclohexene (Fig. 1, Curves 1, 2 and 3) shows the striking similarity between the *cis* compound and cyclo-

---

[1] L. O. Brockway and Paul C. Cross, THIS JOURNAL, **58**, 2407 (1936).

[2] W. G. Young, R. T. Dillon and H. T. Lucas, *ibid.*, **51**, 2528 (1929).

[3] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *ibid.* **58**, 144 (1936).

[4] E. P. Carr and H. Stücklen, *J. Chem. Phys.*, **4**, 762 (1936).

hexene in the first three groups of bands. Not only are the separations of the bands almost identical but the general character is very similar. In the *cis*-butene the average breadth of the sharp bands is of the order of 90 cm.$^{-1}$, in cyclohexene, 110 cm.$^{-1}$, whereas in *trans*-butene-2 the breadth is about 40 cm.$^{-1}$.

A detailed analysis of these spectra will be considered in a separate paper but it is of interest to compare the separation of the band maxima in the two butenes with the Raman lines which have been ascribed to the *cis* and *trans* forms of pentene-2.[5] These absorption bands in the butenes are very sharp and differences between the strongest bands may be measured with an error of less than 10 cm.$^{-1}$. In *cis*-butene the separation between the most intense band of the first and second groups is 1510 cm.$^{-1}$; in *trans*-butene the strong band at 49,480 shows a separation of 1570 cm.$^{-1}$ from the most intense band of the fourth group. In the Raman spectrum of pentene-2 the line which is characteristic of the C=C linkage in all of the olefins is reported as 1658 cm.$^{-1}$ for *cis*-pentene-2 and 1674 cm.$^{-1}$ for the *trans* form so that a vibrational frequency of the order of 1500 cm.$^{-1}$ for the excited molecule would be expected. Thus the values of 1510 and 1570 cm.$^{-1}$ for the *cis* and *trans* butenes in the excited state would show the same relationship as that obtained for the corresponding pentene molecules in their normal state from Raman spectra. The analogous Raman line for cyclohexene is reported as 1646 cm.$^{-1}$;[6] the corresponding vibration for the excited molecule as measured from the ultraviolet spectrum is 1485 cm.$^{-1}$, which gives a close parallelism with the value for *cis* butene-2.

The separation of the narrow bands in the *trans* form as well as the relative intensities of the groups of bands are completely different from the *cis* compound and cyclohexene. These results would seem to give conclusive evidence of the similarity in molecular structure in relation to the double bond which must exist between cyclohexene and the isomer of butene-2 whose spectrum bears so close a resemblance and thus confirms the assignment of the *cis* structure to this higher boiling isomer.

The pentene-2 which was used for earlier measurements[4] had been prepared by dehydration of 3-pentanol with sulfuric acid and was believed to be a mixture of the *cis* and *trans* forms.[7]

Careful refraction with the best columns at our disposal at that time had failed to give any satisfactory separation. When a sample of pentene-2 prepared by the bromo ether synthesis[8] was examined, the spectrum showed a very decided difference in the intensity of the first band as compared with the results previously obtained. The pentene-2 prepared from 3-bromo-2-ethoxypentane and 2-bromo-3-ethoxypentane gives spectra in which the first band is of almost equal intensity with the second group of bands. Comparison with

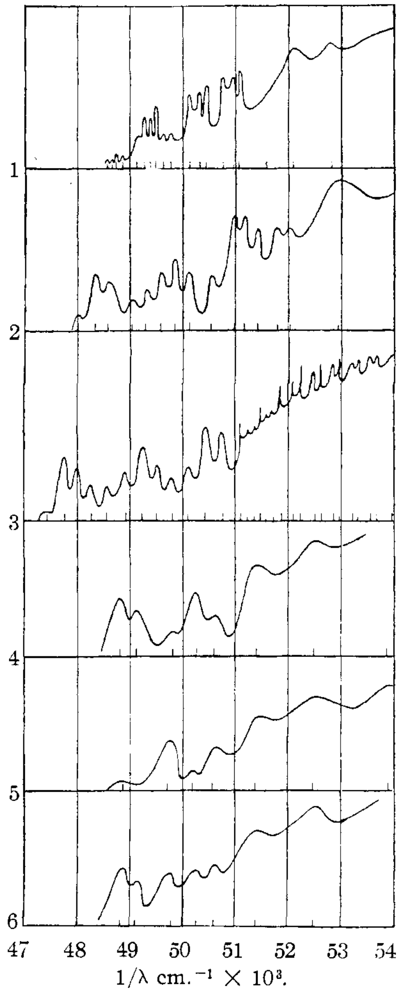

Fig. 1.—Absorption curves of hydrocarbons: 1, butene-2 *trans;* 2, butene-2 *cis;* 3, cyclohexene; 4, pentene-2 *cis*, prepared from pentyne-2; 5, pentene-2 *trans;* 6, pentene-2, 80–90% *cis*, prepared from α-ethylcrotonic acid.

---

(5) Bourguel, Gredy and Piaux, *Compt. rend.*, **195**, 129 (1932).

(6) K. W. F. Kohlrausch and R. Seka, *Ber.*, **68B**, 528 (1935).

(7) Confirmation of this assumption was given by the results obtained on hydrogenation of material prepared in this Laboratory [G. B. Kistiakowsky, *et al.*, THIS JOURNAL, **58**, 137 (1936)].

(8) M. L. Sherrill and E. S. Matlack, *ibid.*, **59**, 2134 (1937).

the absorption curves for the butenes shows that this same intensity relationship exists between the first two groups of bands in *cis*-butene-2, while in the spectrum of the *trans* isomer the first group of bands is extremely weak and the second quite intense. In the heavier pentene molecule the bands are diffuse with no evidence of fine structure, so that this criterion could not be used to differentiate the two isomers. The samples of pentene-2 prepared by the two bromo ether syntheses both gave boiling points slightly higher than the pentene from 3-pentanol; these results pointed to the conclusion that with the pentenes as with the butenes the higher boiling isomer was the *cis* form, and that the pentene preparation from 3-pentanol had given a mixture which was proportionately richer in the *trans* form while the product obtained from the bromo ether synthesis had a considerably larger proportion of the *cis* form.

These conclusions were given further confirmation from absorption spectra measurements of two samples of pentene-2 which on the basis of their methods of preparation[8] should give the two different geometrical isomers of pentene-2. Comparison of the absorption curves of these two compounds (Fig. 1, Curves 4 and 5) shows clearly the similarity between the curves for *cis* butene-2 and the higher boiling isomer of pentene-2 and also between that for *trans* butene-2 and the lower boiling pentene. It is not possible on the basis of these relative intensity measurements to attempt quantitative estimates but it seems reasonably certain since the purity of the butenes was shown to be better than 99.50%[9] and the curves for the pentenes parallel so closely those of the butenes in their intensity relationships that the two pentene preparations represent a purity of 95% or better of each of the two geometrical isomers.

Two different methods were used for preparing the *cis* isomer; the absorption spectrum of pentene-2 obtained by hydrogenation of pentyne-2 is shown in Curve 4, Fig. 1, and from its spectrum this preparation is believed to be practically free from any of the *trans* isomer. The pentene-2 which is prepared by decarboxylation of α-ethylcrotonic acid should be mainly the *cis* form and the curve for this material (Curve 6, Fig. 1) shows a high proportion of this isomer but the intensity of the bands at 49,800 and at 50,600 cm.$^{-1}$ indicates the presence of small amounts of the *trans* isomer.

In the light of these results the plates for the other hydrocarbons in which *cis-trans* isomerism is possible were reëxamined. There were two hydrocarbons, *n*-hexene-3 and *n*-heptene-3, of which the former had been prepared by the bromo ether synthesis and the latter by dehydration of the alcohol with sulfuric acid. There is a marked difference in the relative intensities of the first two bands in these two compounds. The hexene shows the predominance of the *cis* form, the heptene that of the *trans* form, which is in complete agreement with the results obtained with the pentenes when prepared by analogous methods.

## Experimental

**Method and Presentation of Results.**—The experimental procedure for the measurement of the absorption spectra of these hydrocarbons has been described in detail.[4]

The absorption curves show the relative intensities as estimated on the basis of their appearance on the photographic plates. The Schumann plates which were used are made by Hilger and are extremely good but the emulsion is much too uneven to admit of quantitative photometric measurement. The curves were drawn in such a way that if a set of bands, including the minimum between bands, has a higher value on the ordinate than the maxima of another band or set of bands, then the pressure necessary to bring out these stronger bands has been reduced to about 0.1 of the pressure for the less intense bands.

**Preparation of Material.**—The samples of *cis*- and *trans*-butene-2 were kindly given to us by Professor G. B. Kistiakowsky. These hydrocarbons are of the same degree of purity as those used for their hydrogenation experiments: for *cis*-butene-2, b. p. 3.73° (759.8 mm.) and *trans*-butene-2 b. p. 0.96° (760 mm.).

Cyclohexene was prepared in this Laboratory by the dehydration of cyclohexanol.[10]

The method outlined by Kistiakowsky and co-workers[11] was followed and the product which was used for the spectrographic work had the constants: b. p. 82.70 ± 0.05° (760 mm.), $n^{20}_{D}$ 1.4465, $d^{20}_{4}$ 0.8101.

The pentene-2 preparations have been described in detail in the preceding article.[8] The boiling point of the *trans* isomer was 36.25 ± 0.10° at 760 mm.; $n^{20}_{D}$ 1.3790, and $d^{20}_{4}$ 0.6486. For the *cis*-pentene-2 prepared from α-ethyl crotonic acid the constants were: b. p. 36.55 ± 0.05° at 760 mm., $n^{20}_{D}$ 1.3817, and $d^{20}_{4}$ 0.6540. Although the spectrum of this material indicated the presence of some of the *trans* form, the physical constants are believed to be more reliable than those for the *cis* isomer prepared from pentyne-2. It seems probable that the high values for the boiling point and density of this latter product are due to the presence of traces of pentyne-2. Since the boil-

---

(9) Kistiakowsky, *et al.*, THIS JOURNAL, **57**, 880 (1935).

(10) The preparation and purification of cyclohexene and the determination of its physical constants was done by Kate Wilkins as a part of her work for the M. A. degree. This was done under the direction of Prof. M. L. Sherrill of this Laboratory.

(11) Kistiakowsky, *et al.*, THIS JOURNAL, **58**, 140 (1936).

ing point of pentyne-2 is 20° above that of pentene-2, there would not be enough in the vapor to affect the absorption spectrum measurements which are made at a pressure of from 3–6 mm.

The absorption spectra measurements and physical constants for hexene-3 and heptene-3 are reported in earlier publications.[4,12]

## Summary

The ultraviolet absorption spectra of *cis*- and *trans*-butene-2, cyclohexene and different samples of pentene-2 have been examined in vapor phase in the Schumann region. The marked similarity between the spectra of the higher boiling butene-2 and cyclohexene confirms the earlier assignment of the *cis* configuration to this isomer.

The absorption curves for two samples of pentene-2, which from their methods of preparation should give two different geometrical isomers, showed intensity relationships which were entirely analogous to those shown by the *cis* and *trans* isomers of butene-2. These differences were sufficiently marked to serve as a basis for identification of the two isomers; the higher boiling pentene-2 is the *cis* form.

The comparative yields of the two isomers of pentene-2 prepared by four other methods have been estimated from their absorption spectra.

SOUTH HADLEY, MASS. RECEIVED AUGUST 11, 1937

[12] E. P. Carr and G. F. Walter, *J. Chem. Phys.*, **4**, 757 (1936).

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

# The System Lithium Sulfate, Cadmium Sulfate and Water at 30°

BY HELEN PARKS, MILDRED PATTERSON, AND W. C. VOSBURGH

The solubilities and the identity of the solid phases in the system lithium sulfate, cadmium sulfate and water were of interest in connection with the preparation of a modified Weston Cell. Calgagni and Marotta[1] have determined the freezing point curve of the anhydrous system lithium sulfate and cadmium sulfate and found no evidence of a double salt. In the present investigation also no evidence of a double salt was obtained.

Most of the mixtures were prepared from carefully weighed quantities of monohydrated lithium sulfate, selected crystals of hydrated cadmium sulfate and water. The mixtures were rotated in an air-bath at 30 ± 0.05° from one to several days. The agreement of the results when the time of rotation varied showed that equilibrium could ordinarily be attained in one day. The cadmium in the saturated solutions was determined electrolytically[2] and the total sulfate gravimetrically, by the procedure of Friend and Wheat.[3]

Trial of the sulfate determination on known samples of cadmium sulfate gave results about two parts in a thousand too low. There was considerable co-precipitation of cadmium sulfate, and the most nearly correct results were obtained when loss of cadmium oxide was prevented by the avoidance of too high temperatures and sulfuric acid was added to convert any cadmium oxide entirely to sulfate. Ignition was carried out in a muffle at 500°. The cadmium determination was found to give slightly high results, especially with small samples. It is believed that analytical errors were well within ten parts in a thousand.

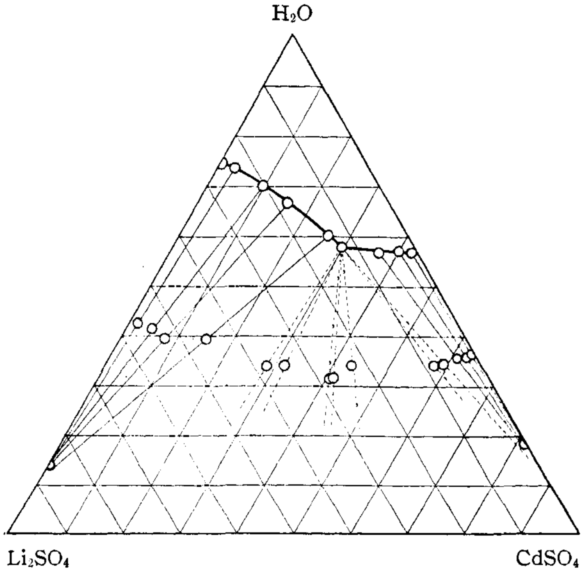

Fig. 1.

The solid material for a few of the mixtures was prepared by slow addition of lithium sulfate to a saturated cadmium sulfate solution. Since the

[1] Calgagni and Marotta, *Gazz. chim. ital.*, **44**, I, 488 (1914).

[2] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929, p. 206.

[3] Friend and Wheat, *Analyst*, **57**, 559 (1932).