

ing-out constant have been calculated for each concentration of salt studied.

The new values for the salting-out constant are

compared with corresponding data at 25 and 18°.

PHILADELPHIA, PA.

RECEIVED JULY 16, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE]

Additional Data on the *cis* and *trans* Isomers of Pentene-2

BY MARY L. SHERRILL AND ELIZABETH S. MATLACK¹

The problem of the synthesis of the two stereoisomers of pentene-2 or of the separation of these from a mixture of the two has been attacked by various investigators with varying degrees of success. The problem has been under investigation in this Laboratory for some years and this report summarizes the results obtained in the synthesis of a pentene-2, which is largely the *cis* form, of one which is largely the *trans* form and for preparations which give mixtures of varying proportions of the two isomers.

The usual methods employed in the preparation of pentene-2 have been the dehydration of 3-pentanol and 2-pentanol and the removal of hydrogen bromide from 3-bromo- and 2-bromopentane.² The physical constants for the pentene obtained from the symmetrical alcohol and bromide by various investigators have been in remarkable agreement. The values found for the pentene from 2-pentanol or 2-bromopentane were in general slightly lower but showed greater variation. This may have been due to traces of pentene-1 which repeated fractionation failed to remove or to varying proportions of the two isomers of pentene-2.

After an unsuccessful attempt to separate the two isomers by fractionation or to bring about any isomerization into the other form Van Risseghem³ concluded that the preparation from 3-pentanol was either the stable isomer or an equilibrium mixture of the two.

Since the physical constants for pentene-2 prepared from α -ethyl- β -bromobutyric acid were identical with those of the pentene obtained from 3-bromopentane, Lauer and Stodola⁴ decided that the product in each case must represent the stable isomer. Since hydrogen bromide is an

effective isomerizing agent and it has been shown⁵ that the hydrogen bromide addition products of tiglic and angelic acids, α -methyl- β -bromobutyric acid, were in each case mixtures of the two stereoisomeric forms, it seems possible that the ethyl derivative would form an analogous mixture in which case the pentene-2 derived from this should be a mixture of the two geometrical isomers.

Applying the method used successfully in the synthesis of *cis*- and *trans*-butene-2^{6,7} Lucas and Prater⁸ prepared pentene-2 from the hydrogen iodide derivatives of the two α -methyl- β -ethylacrylic acids, $C_2H_5CH=C(CH_3)COOH$. The boiling points of the two products were identical but they differed considerably in density and refractive index (Table I). The *cis* form was assigned to the isomer with the higher values which are higher than those previously reported while the values for the *trans* form are practically identical with those obtained by other investigators.

Bourguel and co-workers⁹ have reported the synthesis of *cis*-pentene-2 by reduction of pentyne-2 with colloidal palladium. Comparison of the Raman spectrum of this compound with that of pentene-2 from 3-pentanol¹⁰ showed the latter to contain the characteristic lines of the former and in addition a number of new lines from which it was concluded that the preparation from pentyne-2 was the pure *cis* form and the other a mixture of *cis* and *trans*. The very characteristic line of all aliphatic unsaturated hydrocarbons found at about 1650 cm.^{-1} was at 1658 cm.^{-1} in the spectrum of the *cis* isomer, while in the other there was a line at 1674 cm.^{-1} as well as at 1658 cm.^{-1} . The

(5) Fittig and Pagenstrecker, *Ann.*, **195**, 108 (1879).

(6) Wislicenus, Talbot, Henze and Schmidt, *ibid.*, **313**, 207 (1900).

(7) Young, Dillon and Lucas, *THIS JOURNAL*, **51**, 2528 (1929).

(8) H. J. Lucas and A. N. Prater. Reported to the Organic Division of the American Chemical Society, San Francisco meeting, August, 1935. The authors are indebted to Professor Lucas for the data given in Table I. Private Communication, January, 1936.

(9) Bourguel, *Bull. soc. chim.*, **41**, 1476 (1927); **53**, 496 (1933).

(10) (a) Bourguel, Piaux and Grédy, *Compt. rend.*, **195**, 129 (1932); (b) Van Risseghem, Piaux and Grédy, *ibid.*, **196**, 938 (1933); (c) Grédy, *Bull. soc. chim.*, [5] **2**, 1029 (1935).

(1) Presented before the Organic Division at the Rochester meeting, Sept., 1937.

(2) For bibliography and data to 1929 see papers of Sherrill and co-workers, *THIS JOURNAL*, **51**, 3023, 3034 (1929).

(3) Van Risseghem, *Bull. soc. chim. belg.*, **28**, 53, 187, 288 (1914).

(4) Lauer and Stodola, *THIS JOURNAL*, **56**, 1216 (1934).

TABLE I
 COMPARATIVE DATA FOR PENTENE-2

Investigator	Prepared from	B. p. °C. at 760 mm.	d_{20}^4	n_{20}^D	M. p., °C.
Van Risseghem (1914)	3-Pentanol	36.40 ± 0.05	0.6505 (extrap.)	1.3798 (extrap.)	-147 ± 0.1
Lauer and Stodola (1934)	3-Bromopentane α -Ethyl- β -bromobutyric acid	35.7-35.9 at 743 mm. 35.65-35.70 at 737 mm.		1.3797 1.3795	
Bourguel (1927, 1929)	Pentyne-2	34.2	0.647 at 19°	1.375 at 19°	
Lucas and Prater (1935)	Hydrogen iodide derivatives of α -methyl- β -ethylacrylic acid	36.2 <i>trans</i>		1.3799	-136 → -135
Sherrill and Matlack	α -Ethyl- β -iodobutyric acid α -Ethylcrotonic acid Pentyne-2 3-Bromo-2-ethoxypentane 2-Bromo-3-ethoxypentane 3-Pentanol	36.25 ± 0.10 <i>trans</i> 36.55 ± 0.05 <i>cis</i> 37.8 ± 0.10 <i>cis</i> 36.55 ± 0.05 36.55 ± 0.05 36.25 ± 0.10	0.6486 0.6540 (.6586) .6527 .6523 .6503	1.3790 1.3817 1.3822 1.3807 1.3810 1.3798	-180 → -178

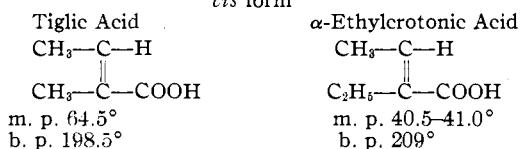
low values for the physical constants (Table I) which were obtained for this *cis*-pentene are not in agreement with those obtained by Lucas and Prater. This may be due to the presence of some pentane in the hydrocarbon prepared by the reduction of pentyne.

The recent assignment by Kistiakowsky¹¹ of the *cis* form to the higher boiling butene-2 (b. p. 3.73°, f. p. -139°) on the basis of the analogy between the heat of hydrogenation of this compound and cyclohexene and the confirmation of this assignment by Brockway and Cross¹² from electron diffraction measurements lends renewed interest to the problem of identifying with certainty the isomers of pentene-2.

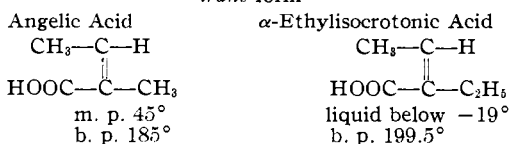
Recent work in this Laboratory has been from two angles: one to synthesize each of the isomers by some method which would give but one isomeric form and the other to separate a mixture of



cis form



trans form



the two isomers by distillation since much better fractionating columns were available than for the earlier work. For the first problem the preparation from the stereoisomeric α -ethylcrotonic acids was undertaken. By analogy to angelic and tiglic acids the configurations shown would be assigned. As with the butenes the *cis* form of pentene-2 should be obtained from the hydrogen iodide derivative of the isocrotonic and the *trans* from the crotonic form.

The preparation of the α -ethylcrotonic acids and their separation by means of their calcium salts was accomplished successfully but was very time consuming. The hydrogen iodide derivative of α -ethylcrotonic acid, as well as the acid itself, is a crystalline solid whereas the isocrotonic forms are liquids and very difficult to purify. It therefore seemed advisable to turn attention to the preparation of large amounts of the solid acid as source material. Pentene-2 was prepared from this acid by two different methods, the first by way of the hydrogen iodide derivative, the second by the catalytic decarboxylation by copper chromite in the presence of quinoline.^{13,14}

The physical constants of pentene-2 prepared by the first method are in general lower than for the material obtained from other preparations (Table I) and comparison of the absorption spectrum in the Schumann region¹⁵ with that of *trans*-butene-2 showed very similar characteristics, indicating it to be the *trans*-form of pentene-2, a result which is in complete accord with the method

(11) Kistiakowsky, Ruhoff, Smith and Vaughan, *THIS JOURNAL*, **57**, 876 (1935).

(12) Brockway and Cross, *ibid.*, **58**, 2407 (1936).

(13) (a) Kinney and Langlois, *ibid.*, **53**, 2189 (1931); (b) Adkins and Connor, *ibid.*, **53**, 1092 (1931).

(14) Taylor and Crawford, *J. Chem. Soc.*, 1130 (1934).

(15) Carr and Stücklen, *THIS JOURNAL*, **59**, 2139 (1937).

of synthesis. On the basis of the results of Taylor and Crawford¹⁴ where isostilbene (*cis*) was obtained from α -phenylcinnamic acid by decarboxylation in the presence of quinoline, the isomer of pentene-2 prepared by this method should be the *cis* form. The predominance of the *cis* form in the product was ascribed by Taylor to the greater stability of that form in quinoline solution. The physical constants of pentene-2 obtained by this method are in close agreement with those given by Lucas and Prater for the *cis* form and absorption spectrum measurements showed a close similarity with those of *cis*-butene-2. Since the physical constants of this compound were not in accord with those reported by Bourguel for the *cis* form, this preparation of pentene-2 by hydrogenation of pentyne-2 was repeated. The amount of material was insufficient to permit of column fractionation so that it seems probable that there were traces of pentyne-2 present which would account for the higher physical constants. The absorption spectrum measurements showed the closest parallelism with *cis*-butene-2 that had been obtained with any of the preparations of pentene-2 so that it is believed that this material is practically free from any of the *trans* isomer. A trace of the acetylenic compound in the liquid would not affect the absorption spectrum since these measurements are made in vapor phase and the amount of the much higher boiling pentyne-2 in the vapor would be entirely negligible. These results confirm Bourguel's assignment of the *cis* form to the pentene-2 prepared from pentyne-2 but indicate that the low boiling point and the low values for index of refraction and density must be in error.

Another approach to the problem was the synthesis of pentene-2 by the action of zinc on 3-bromo-2-ethoxypentane and 2-bromo-3-ethoxypentane. The physical constants of the product in each case are practically identical (Table I), having values somewhat lower than for the *cis* form, which indicate that a fairly large proportion of this isomer was obtained in each of these preparations. Measurements of their absorption spectra gave confirmatory evidence for this conclusion.

An attempt to separate by continuous fractionation through a Fenske column (150 cm. in length) a large quantity of pentene-2 prepared from pentanol-3, which was used so satisfactorily for the butenes¹¹ prepared in an analogous way, was unsuccessful. A small amount of material

(5.2%) distilled below 36.15° and the remainder at 36.25 \pm 0.10°. The physical constants of the latter material are practically the same as those previously reported for pentene-2 from 3-pentanol and from 3-bromopentane (Table I). The values given by Lucas for the *trans* isomer of pentene-2 are almost identical with these but on the basis of our data for *trans*-pentene would represent a mixture containing from 65–75% of the *trans* form. Absorption spectra measurements indicate a mixture containing more of the *trans* than of the *cis* form but these measurements admit of only approximate estimates of proportions. The physical constants of the low boiling fraction, as well as the absorption spectrum measurements, would indicate the presence of a somewhat larger proportion of the *trans* form but the wide boiling range (31.2–36.10°) and the small amount of material obtained make it inadvisable to draw any conclusions.

These results together with those from the absorption spectra measurements in the following paper would seem to justify the conclusion that the products from α -ethylcrotonic acid through its hydrogen iodide derivative is almost completely the *trans* form, that the product from direct decarboxylation by copper chromite is largely the *cis* form, while the semi-reduction of pentyne-2 gives only the *cis* form. On the basis of an index of 1.3790 for the *trans* form and 1.3822 for the *cis*, the proportion of the *cis* form obtained by the different preparations is as follows: from (1) α -ethylcrotonic acid, 85%; (2) the bromoethoxypentanes, 55–60%; (3) pentanol-3, 25%.

The presence of sulfuric acid in the latter preparation may be an influencing factor in favoring the higher proportion of the *trans* isomer but the close agreement of physical constants between this material and those obtained for all earlier preparations of pentene-2 suggests the existence of an equilibrium mixture of constant boiling point.

It is possible that the excess of the *cis* form in the product obtained from the bromo ethers by treatment with zinc may be due to stereochemical effects. The bromo ethers contain two asymmetric carbon atoms and would be a mixture of dextro and levo forms together with a meso form. If one of these stereoisomeric forms should lose the bromine and ethoxy groups more easily than the other, as seems quite possible, this would account for the larger proportion of one form. The low yields which have always been obtained in this reaction give some support to this interpretation.

Experimental¹⁶

Pentene-2 from α -Ethylcrotonic Acid

α -Ethylcrotonic Acid.—This acid was prepared by the methods of various investigators^{4, 17} from α -ethyl- α -hydroxybutyric acid, from its ethyl ester and from the ethyl ester of α -bromodiethylacetic acid. In each case the product was a mixture of varying proportions of the α -ethylcrotonic and the α -ethylisocrotonic acids. The pure solid α -ethylcrotonic acid (m. p. 41.4°) was obtained by fractional crystallization of its calcium salt. This was the acid used for the preparation of the hydrogen iodide derivative. The simplest and most satisfactory method of obtaining the solid acid was by refluxing the α -ethyl- α -hydroxybutyric acid with a few cc. of 48% hydrobromic acid and then distilling the acid at atmospheric pressure. The α -ethylcrotonic acid obtained by this method melted at 40–41°, and was used for the catalytic preparation of pentene-2.

α -Ethyl- β -iodobutyric Acid.—One mole of α -ethylcrotonic acid (m. p. 41.4°) in fourth mole portions was transformed into its hydrogen iodide derivative⁷ (yield 60%, m. p. 28–30°). The α -ethyl- β -iodobutyric acid recrystallized from ligroin melted at 29.5–30°.

Pentene-2 (*trans* Form).—One fourth mole of α -ethyl- β -iodobutyric acid was treated with a cold solution of 0.2 mole of sodium carbonate according to the methods used for the butenes^{3, 7} and for pentene-2 from α -ethyl- β -bromobutyric acid.^{4, 17a} Pentene-2 (33% yield) distilled over below 36°. The crude hydrocarbon had a refractive index n_D^{20} 1.3790, and distilled completely at 36.25 \pm 0.10° at 760 mm., n_D^{20} 1.3790, d_4^{20} 0.6486.

Pentene-2 (85–90% *cis* Form).—A quinoline solution of one mole of α -ethylcrotonic acid (m. p. 40°) in 200 cc., was dropped into 200 cc. of quinoline containing 6 g. of copper chromite, prepared according to Adkins.^{13b} During the addition of the acid (eight to nine hours) the reaction mixture was kept at a temperature of 210°. The pentene-2 distilled almost as rapidly as the solution was added and carbon dioxide was evolved. The hydrocarbon was distilled (36–37°) and collected in a receiver in an ice-bath, the quinoline being condensed (reflux condenser with water at 40–50°) and returned to the reaction flask. After the addition of the acid was complete the reaction mixture was heated at 220–230°, until the reaction seemed complete (three to four hours). The yield of pentene-2 was 70–80%, 300 g. being obtained from five preparations.

In the purification of all of the pentene all reagents were freed from oxygen by a current of nitrogen and all of the apparatus was filled with nitrogen. In this way the pentene-2 was kept free from peroxide and remained so even after several months. The azeotropic distillations were made with absolute methyl alcohol through a Crismer column (150 \times 1.5 cm., 102 turns in the spiral). The hydrocarbon was washed free from the alcohol and dried with calcium oxide. The fractionations of the pentene-2 were made in Fenske columns: A (35 \times 1.5 cm., 1 turn 4-

mm. glass helices); or B (150 \times 2.0 cm., 1 turn 4-mm. glass helices), the reflux ratio being 1:20.

The pentene-2 after an azeotropic distillation was distilled three times through Fenske column A. Between the first and second of these distillations the pentene was cooled to -78° to freeze out any quinoline and was then filtered by suction into a tube at -78° . In the final distillation 60% of the total hydrocarbon distilled above 36°, and of this 35% at 36.0–36.5°, with a density d_4^{20} 0.6532, and refractive index n_D^{20} 1.3810, the remaining 65% had the following physical constants: b. p., 36.55 \pm 0.05°, at 760 mm., d_4^{20} 0.6540, n_D^{20} 1.3817. The absorption spectra measurements and the physical data indicate this to be 85–90% *cis*-pentene-2.

Pentene-2 from Pentyne-2

Pentyne-2.—One mole of 2,3-dibromopentane (b. p. 62.5 \pm 0.05° at 10 mm., d_4^{20} 1.6744, n_D^{20} 1.5082) heated with alcoholic potassium hydroxide gave a 70% yield of pentyne-2. This fractionated through the Fenske column A distilled below 55.6°, 80% with b. p. 55.0 \pm 0.20° and n_D^{20} 1.4050.

Pentene-2 (*cis* Form).—The pentyne-2 (0.25 mole) was hydrogenated in an alcohol-water solution with colloidal palladium.⁹ The pentene-2 with alcohol distilled from the mixture through a Vigreux column between 34–36°. The hydrocarbon (60% yield) freed from alcohol had an index, n_D^{20} 1.3825. The pentene was distilled through a Vigreux distilling flask, 95% of it having these physical constants: b. p. 37.8 \pm 0.10°, at 760 mm., d_4^{20} 0.6586, n_D^{20} 1.3822. The absorption spectrum of this compound resembled most closely that of *cis*-butene-2 and is believed free from the *trans* form. Due to the presence of traces of pentyne-2 the physical constants may be high, especially the density which was determined on the material after the absorption spectrum measurements had removed a considerable quantity of the pentene-2 vapor, thereby leaving the residue richer in the impurity.

Pentene-2 from 2-Bromo-3-ethoxy- and 3-Bromo-2-Ethoxypentane

2-Bromo-3-ethoxypentane.—This compound was synthesized by the Boord synthesis^{18, 19} in an average over-all yield of 37.5% (total yield 3350 g.). The physical constants for this compound are: b. p. 50.6 \pm 0.20°, at 7 mm., d_4^{20} 1.1746, n_D^{20} 1.4443.

3-Bromo-2-ethoxypentane.—This compound was prepared similarly with an average over-all yield of 58.5% (total yield 5476 g.). The physical constants obtained for this are: b. p. 47.5 \pm 0.10°, at 7 mm., d_4^{20} 1.1830, n_D^{20} 1.4472.

Pentene-2 (55–60% *cis* Form).—The bromoethoxypentanes were transformed into pentene-2 (55% yield, total weight 1000 g.) by the method given previously.^{19b} The hydrocarbon from each bromoethoxypentane was distilled twice azeotropically and then fractionated through the Fenske column B; 95% of the total distilled at 36.55 \pm 0.05°. All fractions except the last were practically identical in physical properties (Table I). The last frac-

(16) Acknowledgment is hereby made for the assistance in the preparative work of E. J. Cook, M. E. Marshall, L. S. Taylor, H. L. West, and E. A. Winter.

(17) (a) Fittig and Howe, *Ann.*, **200**, 21 (1880); (b) Fittig, Borstelmann and Lurie, *ibid.*, **334**, 101 (1904); (c) Blaise and Bagard, *Ann. chim.*, [8] **11**, 111 (1907); (d) von Auwers, *Ann.*, **432**, 46 (1923).

(18) (a) Swallen and Boord, *This Journal*, **52**, 651 (1930); (b) Shoemaker and Boord, *ibid.*, **53**, 1505 (1931).

(19) (a) Sherrill, Smith and Thompson, *ibid.*, **56**, 611 (1934); (b) Sherrill and Walter, *ibid.*, **58**, 742 (1936).

tion in each case had slightly higher values, d^{20}_4 0.6535, n^{20}_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. $115.65 \pm 0.05^\circ$ at 760 mm., d^{20}_4 0.8219, n^{20}_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 $31.4 \pm 0.20^\circ$ 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 $36.25 \pm 0.10^\circ$. 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 investiga-

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

tors. 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.

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[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 collaborators² from chemical evidence and is in agreement with that given by Kistiakowsky and collaborators³ 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 hydrocarbons⁴ in the region between $\lambda = 2400$ and 1600 \AA . 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 \AA . may be ascribed to an electronic excitation which is characteristic of the 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).