

tained. This was taken up in ether, dried, evaporated to dryness and treated with thionyl chloride. When the thionyl chloride solution was poured into an excess of iced ammonium hydroxide, the precipitate was barely visible and embedded in a yellow oil. When washed with ether it melted at 165–170° and lowered the melting point of the 167° amide thirty degrees. The melting point of a mixture with the 232° amide was 180–190°. Apparently the substance was not the amide of hexahydro-mesitylene carboxylic acid. No conclusions can be drawn from this evidence as to the structure of the peroxide, since apparently most of the material gave up its oxygen without cleavage. The remaining neutral material when treated with hydroxylamine deposited a trace of crystalline material which analysis showed to be a hydrocarbon, m. p. 200–205°.

Anal. Found¹⁷: C, 92.64; H, 6.83. No other crystalline material could be isolated.

Summary

The preparation and properties of one of the six possible geometric isomers of hexahydroacetomesitylene are described.

Investigation of this isomer of hexahydroacetomesitylene and some of its derivatives indicates that this particular configuration of the trimethylcyclohexane ring offers slightly less hindrance to the reactions of a ketone group adjacent to the ring than does the mesitylene nucleus.

RECEIVED DECEMBER 8, 1939

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Separation of the Isomeric Hexenes by Batch Fractionation

BY ARTHUR ROSE

The maximum sharpness of separation between any two components in a batch fractionation may be estimated by an extension of the reasoning of Sydney Young¹ and of Rayleigh² as will soon be described in detail elsewhere.³ The present paper applies this line of reasoning to the separation of the isomeric hexenes so as to obtain a definite idea of the fractionating efficiency required and the results to be expected in attempts at such separations.

The Vapor Pressure Ratios of the Hexenes.—

In order to estimate the maximum possible sharpness of separation for any pair of substances it is necessary to know the vapor pressure ratio (α) for the pair. These may be obtained for the hexenes by using the boiling points of Schmitt and Boord⁴ and the boiling point correction method cited by Eaton.⁵ Thus 2-ethyl-1-butene boils at 66.45° at 760 mm. while 3-hexene boils at 66.8°. At this temperature the b. p. correction would be about 0.042° per mm., so that at 66.8° the vapor pressure of 2-ethyl-1-butene must be about 768 mm. and α for this pair must be about $768/760 = 1.011$.

(1) Sydney Young, "Distillation Principles and Processes," Macmillan Co., London, 1922, p. 117.

(2) Walker, Lewis, McAdams and Gilliland, "Principles of Chemical Engineering," p. 532, McGraw-Hill Book Co., New York, N. Y., 1937; also Badger and McCabe, "Elements of Chemical Engineering," McGraw-Hill Book Co., Inc., New York, N. Y., 1936, p. 336.

(3) Arthur Rose and L. M. Welshans, *Ind. Eng. Chem.*, **32**, May (1940).

(4) Schmitt and Boord, *THIS JOURNAL*, **54**, 751 (1932); **53**, 2427 (1931).

(5) E. S. Beale, "Science of Petroleum," Vol. II, Oxford University Press, Oxford, 1937, p. 1280, etc.

The values in Table I were obtained in a similar manner. In every case only three significant figures are retained but in dropping excess figures the value of α was increased, except for pair A, so the other pairs are actually more difficult to separate than the values of α indicate.

TABLE I

Hexene pair	Alpha
(A) 2-Ethyl-1-butene and 3-hexene	1.01
(B ₁) 2-Methyl-2-pentene and 3-methyl-2-pentene- <i>trans</i>	1.02
(B ₂) 3-Hexene and 2-methyl-2-pentene	1.02
(B ₃) 3-Methyl-2-pentene- <i>cis</i> and 3-ethyl-1-butene	1.02
(C) 2-Ethyl-butene-1 and 2-methyl-2-pentene	1.03
(D) 3-Methyl-2-pentene- <i>cis</i> and - <i>trans</i>	1.07

The estimates of maximum sharpness of separation to be given below assume that α is constant over the temperature range and concentrations involved in the distillations. The temperature ranges involved are so narrow that the variation in α from this source may certainly be disregarded. The conclusions of Beatty and Calingaert⁶ make it reasonable to assume that none of the hexene mixtures would depart sufficiently from ideality to alter the general nature of the conclusions to be drawn in this paper.

Distillation Curves to be Expected.—It can be shown³ that a distillation curve with a maximum sharpness of separation approximately like that

(6) H. A. Beatty and G. Calingaert, *Ind. Eng. Chem.*, **26**, 504 (1934).

of curve *E* in Fig. 1 would be obtained if the column employed had only a sufficient number of plates (n) so that the over-all fractionating factor (α^n) would be 1.25. Thus α^n would need to be

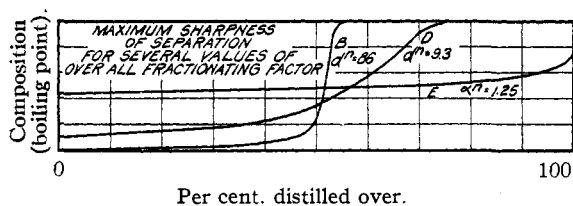


Fig. 1.

1.25 where α is the vapor pressure ratio of the pair being separated and n is the equivalent number of plates used in the separation. The zero of the horizontal coordinates on the figure coincides approximately with the beginning of the plateau of the *lower boiling* component, and the 100 of the horizontal coordinates coincides approximately with the end of the plateau of the higher boiling component of the pair being separated. On this basis the number of plates required to obtain a separation like that indicated by curve *E* would be as listed in Table II.

TABLE II

Pair	Plates required for curve E
A	22
B	11
C	8
D	4

In other words the number of plates indicated would lead to no noticeable separation.⁷ In Table III, from similar⁸ calculations, are given the number of plates necessary to obtain the reasonable separation indicated by curve *D* or the sharp separation of curve *B* of Fig. 1.

TABLE III

Pair	α	Plates required	
		Curve D $\alpha^n = 9.3$	Curve B $\alpha^n = 86$
A	1.01	224	450
B	1.02	112	224
C	1.03	75	150
D	1.07	33	66

Interpretation of Curves.—In studying curves *B*, *D* and *E* of the figure it should be recalled that the vertical coordinates have been greatly stretched and the horizontal coordinates compressed. Actually for the case of the hexenes under discussion the entire vertical scale of the

figure represents only about 0.3, 0.6, 0.9, 2.0°, for pairs *A*, *B*, *C* and *D*, respectively. As stated above, the entire length of the horizontal scale of the figure corresponds approximately with the distance from the beginning of the plateau of the low boiler to the end of the plateau of the high boiler of the particular pair under discussion. Thus curve *E* indicates no separation at all. Curve *D* represents a separation in which the intermediate fraction is about 40% of the combined amount of the two components being separated, and curve *B* a good separation in which the intermediate fraction is only about 5% of the combined amount of the two components being separated.

Comparison with Results of Goldwasser and Taylor.—These authors⁸ have recently described the separation of isomeric hexenes with a modified Podbielniak-Simons type column, and it is of interest to compare their results with those to be expected from the above calculations. The comparison must be approximate because the small scale of the distillation curves in their paper makes it difficult to interpret them accurately. One case has been worked out in some detail. In Fig. 2 of the paper by Goldwasser and Taylor there is shown the separation of a hexene boiling at 67.5° from another boiling at 67.8°. The value of α for such a pair would be approximately 1.01. The combined amount of these two components corresponds to a length of 16.8 mm. on their figure, the length of the intermediate cut is about 3 mm., so the intermediate cut is about 18% of the total amount of the two components. Assuming a 95% purity along the plateaus as stated by Goldwasser and Taylor, this would require⁸ α^n to be about 70, and with $\alpha = 1.01$ it would require about 425 plates to achieve this separation, if it was carried out in the absence of other components and under total reflux in a column with zero holdup. The assignment of 3 mm. to the length of the intermediate cut is rather arbitrary but even if 6 mm. were assigned the minimum plates required would be 350. The separations of hexene pairs boiling at 67.8 and 68.0°, and 67.2 and 67.5° would require a similar efficiency; in fact, all except the first four pairs shown on this figure would require in excess of 200 theoretical plates for the separations indicated. Deviations from ideality and the presence of additional components would not be expected to change the order

(7) Data obtained in this Laboratory since these calculations were made confirm these predictions; see Whitmore, *et al.*, **62**, 795 (1940).

(8) S. Goldwasser and H. S. Taylor, *THIS JOURNAL*, **61**, 1751 (1939).

of magnitude of the number of plates required, but consideration of the holdup and the 30 to 1 reflux ratio actually used in these distillations would certainly increase the estimates considerably.⁹

Consideration of Holdup and Reflux Ratio.—

All the above computations are on the assumption that reflux was nearly total and that holdup was zero so that the conclusions are for maximum sharpness of separation and minimum plates required. No statement of the holdup in the Podbielniak-Simons-Taylor⁸ column is given but it must be appreciable compared with the amount of any one component and quite large compared

(9) Arthur Rose, L. M. Welshans and H. H. Long, *Ind. Eng. Chem.*, **32**, May (1940).

with the amounts of the components present in small amount so that the separations involving these would be expected to be much less sharp than the above discussion indicates.

Summary

Calculations have been made to show that a minimum of 400 or more theoretical plates are required for sharp separation of certain close boiling hexenes, and that the use of a fractionating column with a small number of theoretical plates can produce no appreciable separation in such cases even with low holdup and high reflux ratio.

STATE COLLEGE, PA.

RECEIVED NOVEMBER 20, 1939

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Attempted Separation of Isomeric Hexenes by Fractional Distillation

BY FRANK C. WHITMORE, M. R. FENSKE, D. QUIGGLE, H. BERNSTEIN, T. P. CARNEY, S. LAWROSKI, A. H. POPKIN, R. B. WAGNER,^{1a} W. R. WHEELER AND J. S. WHITAKER

These laboratories have long been interested in the separation of difficult mixtures, especially of olefins, by fractional distillation. Consequently, it was hoped that the recent work by Goldwasser and Taylor¹ would point the way to separations hitherto not possible. We are indeed sorry to have to report that this hope has not been realized.

The Podbielniak-Simons-Taylor column¹ seems to be an excellent one of its type but has an efficiency of only about fifteen theoretical plates. Whereas the published results¹ seem to indicate a successful separation of six hexenes with a total boiling point spread of 2.5°, we have found it impossible to obtain separations even with two binary mixtures of pure hexenes having boiling point spreads of 1.5 and 2.7°, or with a ternary mixture having an over-all spread of 2.7°.

It is interesting to note that a calculation of the column efficiency needed to effect the indicated separation of the six hexenes¹ gives a value of at least 450 theoretical plates.²

Goldwasser and Taylor¹ use the boiling point and density to identify an olefin. This is at least difficult because of the conflicting values recorded for these constants.

Inconsistencies appear in the paper.¹ Thus,

(1) Goldwasser and Taylor, *THIS JOURNAL*, **61**, 1751, 1762, 1766 (1939).

(1a) Submitted in partial fulfillment for the Ph.D. degree.

(2) Rose, *THIS JOURNAL*, **62**, 793 (1940).

on pp. 1753-1754 there is a confusion of the *cis* and *trans* forms of 3-methyl-2-pentene. Agreement with the work of van Risseghem³ is cited "to emphasize the confidence that may be placed in the fractionations obtained." As a matter of fact such agreement is lacking. The authority cited³ obtained three fractions in the careful distillation of the hexenes from 3-methyl-3-pentanol, *viz.*: I, b. p. 65.1-65.7°; II, 67.2-67.8°; III, 69.9-70.2°. She states that I and III are stereoisomers of 3-methyl-2-pentene and that II is a mixture containing some of the methylene isomer. The boiling points given by Goldwasser and Taylor (Table 1a¹) for the two 3-methyl-2-pentenes are 65.7-66.2° and 67.6-68.2°. These differ from those actually reported by van Risseghem,³ which are 65.1-65.7° and 69.9-70.2°.

In certain cases where geometrical isomerism is possible, one constant used for identification¹ belongs to the *trans* form, while the other belongs to the *cis*. The literature values given for the isomers of 3-hexene are: *cis*, b. p. 70-71.2°, *d*₂₀⁴, 0.7190; *trans*, 67.3-67.5°, 0.7170. However, in the dehydration of 1-hexanol, 3-hexene was identified by the observed values, 67.5° and 0.720.

For 4-methyl-2-hexene the accepted values⁴ are:

(3) Van Risseghem, *Bull. soc. chim. Belg.*, **47**, 47 (1938).

(4) Egloff, "Physical Constants of Hydrocarbons," Reinhold Publishing Company, New York, 1939. Doss, "Physical Constants of Principal Hydrocarbons," The Texas Company, New York, 1939.