at different stages in the purification, the first after the azeotropic distillation and the other two after each distillation through the Fenske column. The absorption curves are all identical whereas in the case of other unsaturated hydrocarbons it has been found more difficult to obtain completely reproducible curves since the ultraviolet absorption spectrum is a quite delicate test for the presence of impurities in these compounds.

The ultraviolet absorption measurements were made with a Hilger quartz spectrograph (E-2), using a condensed spark between copper electrodes as the light source. The measurements were made and the extinction coefficient calculated according to the photographic method developed by Henri.[16] Baly tubes of fused quartz were used for all the measurements, the length of the absorbing column being varied from 7 to 0.1 cm. The pure liquid hydrocarbon was used for the determination of extinction coefficients corresponding to log $\epsilon = -2.0$ to -0.7, while hexane solutions varying from 0.74 to 0.01 molar were used for the other measurements. Each curve is based on at least sixty experimental points but the points are not shown on the curve since they are so closely spaced as to give practically a continuous line.

Summary

1. 1-Bromo-2-ethoxy-2-methylbutane has been prepared and its physical constants determined.

2. 2-Methylbutene-1 has been synthesized, its physical constants determined, its absorption spectrum measured and its dibromide prepared.

SOUTH HADLEY, MASS. RECEIVED NOVEMBER 15, 1935

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[16] V. Henri, "Études de Photochimie," Gauthier-Villars et Cie., Paris, 1919. *Cf.* E. P. Carr, THIS JOURNAL, **51**, 3041 (1929).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE]

The Raman Spectra of 2-Methylbutene-1 and 2-Methylbutene-2

BY DOROTHY D. THOMPSON[1] AND MARY L. SHERRILL

The Raman spectra of pentene-1, pentene-2 and a fairly pure sample of 2-methylbutene-2, have been determined by Bourguel and Piaux.[2] Because of the strong line around 1600–1700 cm.$^{-1}$ occurring in the Raman spectra of these compounds, Bourguel[2] suggested that the Raman spectra of these hydrocarbons be used for purposes of identification and analysis. The spectrum of pure 2-methylbutene-1, however, has not been determined previously. Bourguel and Piaux[2] determined the spectra of the high and the low fractions of the hydrocarbon obtained in the preparation of 2-methylbutene-2 by the dehydration of *t*-amyl alcohol. The spectrum of the low fraction showed two lines in the 1650 cm.$^{-1}$ region. The same two lines were present in the spectrum of the high fraction, but that at 1653 cm.$^{-1}$ was very weak and that at 1679 cm.$^{-1}$ was much stronger. It was assumed that the high fraction was almost pure 2-methylbutene-2 and the lower fraction a mixture of this with 2-methylbutene-1. Thus the spectrum of the latter was determined by a comparison of the spectrum of the low fraction with that of the high fraction. In the present investigation the Raman spectra of the high and low fractions of the hydrocarbons obtained from dehydrating tertiary amyl alcohol have been compared with that of synthetic 2-methylbutene-1.[3]

The spectrum of the pure compound showed all the lines assigned to it by Bourguel and Piaux[2] except one (939 cm.$^{-1}$) as well as several others which overlapped the lines due to 2-methylbutene-2. In the case of both the low and the high fractions of the hydrocarbons from *t*-amyl alcohol more lines were found than were reported by Bourguel. The line corresponding to a shift of 1656 cm.$^{-1}$ (characteristic of 2-methylbutene-1) was found only very faintly on one overexposed plate of the high fraction whereas in the low fraction the intensity of this line is about twice as great as that at 1680 cm.$^{-1}$ (characteristic of 2-methylbutene-2).

Experimental

Apparatus.—A Hilger E-439 spectrograph (F/3) was used for these determinations. The dispersion is small but the resolution is good. Three mercury arcs (High and Pool) running vertically on 110 d. c. at a steady current of 3.5–4 amperes and cooled by an electric fan were the source of light. The Raman tube was of the Wood type with a jacket for filter solutions as well as a cooling jacket.

The photographs were made with Eastman spectrographic plates. The "O" plates for excitation by 4047 Å. and "G" for excitation by filtered 4358 Å. mercury light. The slow but fine-grained "III" plates were employed wherever possible, but "I-O" and "I-G" were

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[1] The Raman spectra measurements were made by D. D. Thompson in the Research Laboratory of Organic Chemistry of Massachusetts Institute of Technology and acknowledgment of this courtesy is hereby made.

[2] Bourguel and Piaux, *Bull. soc. chim.*, **51**, 1051 (1932).

[3] Sherrill and Walter, THIS JOURNAL, **58**, 742 (1936).

used where exposures of greater than ten hours would be required if the slower plates were used. For example, the volume of the low fraction from the dehydration of tertiary amyl alcohol was so small that it was necessary to use a small tube, thus decreasing the intensity of the Raman light (see Plate 1-B). For filters, Corning "Greenish Nultra" glass or a saturated solution of sodium nitrite were used to cut out ultraviolet light, quinine sulfate to remove 4047 Å. light and Corning "Red-Purple Ultra" to weaken 4358 Å. mercury light.

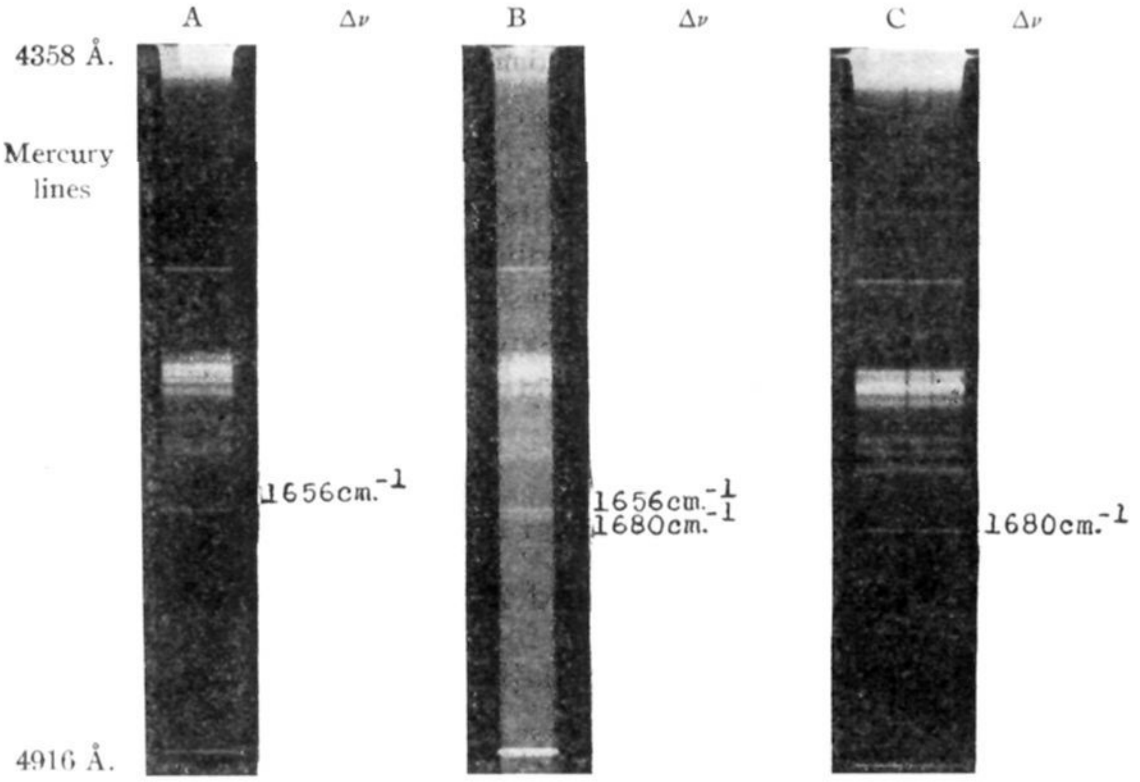

Plate 1.—Raman spectra of 2-methylbutene-1 and 2-methylbutene-2. These prints are enlarged seven times from the original plates.

A. 2-Methylbutene-1 (b. p. 31.05° at 760 mm., n^{20}_D 1.3777, d^{20}_4 0.6504), $\Delta\nu$ = 1656 cm.$^{-1}$, time, 8 hours, Plate III-0, filter, Greenish Nultra.

B. 2-Methylbutene-1 and 2-methylbutene-2 (b. p. 31.8–32.4° at 760 mm., n^{20}_D 1.3806, d^{20}_4 0.6570, low fraction from dehydration of tertiary amyl alcohol), $\Delta\nu$ = 1656 cm.$^{-1}$ and 1680 cm.$^{-1}$, time, 3 hours, Plates I-G, filter, sodium nitrite solution.

C. 2-Methylbutene-2 (b. p. 38.2–38.4° at 760 mm., n^{20}_D 1.3877, d^{20}_4 0.6625, high fraction from dehydration of tertiary amyl alcohol), $\Delta\nu$ = 1680 cm.$^{-1}$, time, 9 hours, Plate III-0, filter, Greenish Nultra.

The plates were measured on a Hilger comparator read to 0.001 mm. The wave lengths were determined by reference to three deviation curves (3984–4108 Å., 4108–4339 Å., and 4339–4916 Å.) made from the spectrum of an iron arc. The wave numbers were corrected to vacuum by reference to Kayser's "Tabelle der Schwingungszahlen."[4] The error in reading the sharp relatively strong lines on the fine grained plates was less than ±1 cm.$^{-1}$, that for the weak diffuse lines on the coarse grained plates was sometimes as large as ±5 cm.$^{-1}$. The data for the Raman spectrum of synthetic 2-methylbutene-1 are summarized in Table I and one photograph is given on Plate 1-A. The data for the Raman spectrum of the low fraction hydrocarbon from tertiary amyl alcohol are summarized in Table II and Plate 1-B. A few lines reported by Bourguel as excited only by 4358 Å. line were found excited, also, by 4047 Å. One line ($\Delta\nu$ = 288 cm.$^{-1}$) not reported by Bourguel was found not only in the mixture, but also in the spectrum of the synthetic 2-methylbutene-1. Two lines reported by Bourguel are missing ($\Delta\nu$ = 888 cm.$^{-1}$ weak, and $\Delta\nu$ = 939 cm.$^{-1}$ very weak). The latter did not appear in any of the plates of this investigation, but $\Delta\nu$ = 890 cm.$^{-1}$ was found in the spectrum of 2-methylbutene-1.

The data for the Raman spectrum of 2-methylbutene-2 (high fraction hydrocarbon from *t*-amyl alcohol) are given in Table III and one photograph on Plate 1-C which shows very clearly the line 1680 cm.$^{-1}$ characteristic of 2-methylbutene-2. On a greatly overexposed plate a very faint line could be detected which corresponded to a Raman shift of 1656 cm.$^{-1}$ (characteristic of 2-methylbutene-1) and a line not reported by Bourguel corresponding to a shift of 1051 cm.$^{-1}$ excited by both 4047 and 4358 Å. appeared on this plate.

A comparison of the spectrum of the low fraction hydrocarbon with that of the high fraction hydrocarbon and that of pure 2-methylbutene-1 shows that undoubtedly this low fraction is a mixture of 2-methylbutene-1 and 2-methylbutene-2 and that the high fraction is 2-methylbutene-2 with only a trace of 2-methylbutene-1 present.

Data

TABLE I

2-METHYLBUTENE-1

252 (0) (e); 393 (2b) (a, c, e); 433 (2b) (e); 485 (1) (e); 530 (1) (e); 709 (1) (e); 773 (5) (a, e); 890 (2) (e); 964 (1) (e); 1020 (1b) (a, e); 1091 (3) (e); 1390 (0) (a, e); 1413 (3) (a, e); 1433 (3) (a, e); 1654 (5) (a, e); 2856 (3) (a); 2893 (5b) (a, b); 2917 (4) (a); 2942 (4) (a); 2971 (2) (a); 2984 (3) (a).

TABLE II

2-METHYLBUTENE-1 AND 2-METHYLBUTENE-2

258 (1) (e); 288 (0) (a, e); 388 (1) (a, e); 446 (0) (e); 530 (2) (e); 771 (7) (a, e); 800 ± 5 (00) (a, e); 1011 (0) (e); 1088 (4) (a, e); 1341 (0) (a, e); 1385 ± 4 (3b) (a, b, e); 1411 (0) (a); 1432 (0) (a); 1442 (0b) (e); 1454 (0) (a); 1656 (4) (e); 1680 (2) (e); 2732 (0b) (a); 2861 (3) (a); 2883 (5) (a); 2921 (20b) (a, b); 2945 (3) (a); 2970 (4) (a); 2983 (4) (a); 3083 (0) (a).

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[4] Kayser, "Tabelle der Schwingungszahlen," Verlag S. Hirzel, Leipzig, 1925.

TABLE III

2-METHYLBUTENE-2

255 (0b) (e); 386 (2) (a, e); 443 (2) (a, e); 526 (3) (a, e); 767 (6) (a, b, e); 800 (1b) (a,[a] e); 1052[a] (00) (a, e); 1337 (3) (a, e); 1383 (4) (a, b, e); 1435 (1) (a, e); 1448 (8) (a, e); 1654[a] (000) (e); 1680 (8) (c,[a] d,[a] e); 2732 (2) (a); 2861 (8) (a); 2885 (2) (a); 2919 (20b) (a); 2972 (7) (a); 3026 (1) (a); 3060 (1) (a).

[a] These lines occur on the overexposed plate only.

In the tables, the data are summarized as follows. A weighted average of the Raman shift as determined from plates taken with filtered and unfiltered radiation is followed by a number indicating the relative intensity of the line, and letters indicating the mercury lines by which it was excited. a = 4047 Å., b = 4077 Å., c = 4339 Å., d = 4347 Å., e = 4358 Å. line. The intensity estimated visually is indicated 000 for the lowest, by 10 for very strong, and by 20 for a few exceptionally strong lines. The letter b following an intensity number indicates a broad line.

Summary

The Raman spectrum of synthetic 2-methylbutene-1 has been photographed.

The Raman spectra of the low and the high fractions of the hydrocarbon obtained by the dehydration of tertiary amyl alcohol show the former to be a mixture of 2-methylbutene-1 and 2-methylbutene-2, while the latter is practically pure 2-methylbutene-2.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

Aliphatic Diazo Compounds. II. Phenyl-alpha-naphthyldiazomethane

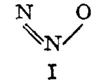
BY GORDON C. HARROLD AND MARTHA G. HEMPHILL WITH FRANCIS EARL RAY

Since Levene and Mikeska[1] first prepared aliphatic diazo esters that seemed to be optically active, a large amount of work has been done in an effort to decide whether an asymmetric carbon atom attached to an amino group retains its asymmetry when the amino group is converted into the diazo derivative. Noyes and Chiles[2] extended and later Lindemann[3] apparently confirmed these results.

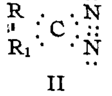
The decomposition of various amino and diazo camphor compounds has been studied also in an attempt to elucidate the structure of the diazo group.[4]

More recently Weissberger[5] has shown that the *p*H of the solution influences the optical activity of the products of decomposition of diazo esters and that these products (hydroxy compounds) were found sufficient to account for *all* the activity previously attributed to the diazo esters. There is a certain similarity between the intermediate compound postulated by Weissberger and that of Noyes and Kendall.[4b] Noyes and Meitzner,[4e] however, point out that in the decomposition of aminolauronic acid a Walden inversion occurs. This means that neither mechanism is adequate to explain the formation of these diazo compounds and their complex decomposition products.

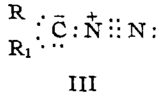
Even if we accept Weissberger's researches as invalidating the conclusions drawn from the previous work on diazo esters, we do not necessarily have to conclude that all aliphatic diazo compounds have the ring structure II. The aliphatic diazo esters are a special class of diazo compounds. It is well known that a carbonyl or ester group contributes greatly to the stability of the diazo grouping.[6] The reason for this may well be ascribed to a tautomeric ring formation involving the nitrogen, oxygen and carbon atoms, I. This compound would be optically inactive, due to the presence of the ethylenic double bond but it would not give any evidence that would enable us to decide between the Curtius, II, and the Angeli–Thiele, III, formulas.[7] (Compare Noyes and Meitzner.[4e])



I



II



III

We have sought, in the present work, a compound which would be without the polar groups

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(1) Levene and Mikeska, *J. Biol. Chem.*, **45**, 592 (1921); **52**, 485 (1922).

(2) Chiles with Noyes, THIS JOURNAL, **44**, 1798 (1922).

(3) Lindemann, Wolter and Groger, *Ber.*, **63**, 702 (1930).

(4) (a) Noyes and Skinner, THIS JOURNAL, **39**, 2692 (1917); (b) Kendall with Noyes, *ibid.*, **48**, 2404 (1926); (c) F. E. Ray, *ibid.*, **52**, 3004 (1930); (d) Heubaum and Noyes, *ibid.*, **52**, 5070 (1930); (e) Noyes and Meitzner, *ibid.*, **54**, 3768 (1932).

(5) Weissberger, *Ber.*, **64B**, 2896 (1931); *ibid.*, **65B**, 265 (1932); *ibid.*, **66**, 559 (1933).

(6) Staudinger, *Ber.*, **37**, 1295 (1904).

(7) Bradley and Robinson, THIS JOURNAL, **52**, 1558 (1930).