either starch or cellulose in catechol was found. The small ΔT which was observed at first in both cases disappeared in a few hours and was undoubtedly due to moisture.

Except where there is definite evidence for chemical degradation, none of these polymers shows anomalous behavior to the degree exhibited by the products derived from coal. However, both the lactide and the cumar resin polymers show significant differences in the two solvents which cannot be ascribed to any known chemical reaction.

The small ΔT observed in diphenyl for the products derived from coal can be explained by assuming that a large part of the solute is colloidally and not molecularly dispersed, but such a distinction, in a system of this type, between a colloid particle and a macromolecule appears of little significance. The large values of ΔT in catechol may ultimately be found to be due to degradation of the polymer by some chemical reaction, but if such a mechanism is later discovered it will not affect the conclusion that these primary breakdown products of a Pittsburgh seam bituminous coal, the regenerated humic acids and the bitumens, must be polymers built up of relatively small units which are held together by such weak forces that as mild a "chemical reagent" as fused catechol can effect degradation. It is probable that the original coal itself is such a polymer, but degradation of coal by solvents only becomes considerable at relatively high temperatures.

Summary

Cryoscopic determinations in catechol and, where solubility permitted, in diphenyl, of a number of polymeric solutes have been made. Except where there is definite evidence of chemical degradation, none of these polymers shows anomalous behavior to the degree exhibited by products derived from coal. It has been pointed out that the cryoscopic behavior of these primary degradation products of coal shows them to be polymers built up of relatively small units.

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF MOUNT HOLYOKE COLLEGE]

Preparation and Physical Constants of 2-Methylbutene-1

BY MARY L. SHERRILL AND GERTRUDE F. WALTER[1]

Unsymmetrical methylethylethylene, 2-methylbutene-1, has been reported by a number of investigators as one of the products of dehydration of commercial amyl alcohol,[2] active amyl alcohol,[3] and tertiary amyl alcohol.[4,5] It has also been obtained from the iodide derivative of active amyl alcohol,[6,7] from tertiary amyl iodide[8] and by the electrolysis of sodium dimethyl glutarate.[9] In no case was pure 2-methylbutene-1 obtained but the boiling point of the compound was shown to be within the 31–34° range.

An investigation of the ultraviolet absorption spectra of olefins has been in progress in this Laboratory for several years. Trimethylethylene has been prepared from tertiary amyl alcohol by the action of iodine, of oxalic acid and of 15% sulfuric acid. In every case a low-boiling fraction, b. p. 30–34°, $n^{20}D$ 1.3774–1.3809, d^{20}_4 0.6505–0.6570,[10] was obtained but careful fractionation failed to separate pure 2-methylbutene-1 and the preparation of that hydrocarbon by the nuclear synthesis of olefins developed by Boord and co-workers[11] was undertaken. The reactions involved in this synthesis are as follows

$$CH_3CHO + C_2H_5OH + HCl \longrightarrow CH_3CHClOC_2H_5 + H_2O \quad (1)$$

$$CH_3CHClOC_2H_5 + Br_2 \longrightarrow CH_2BrCHBrOC_2H_5 + HCl \quad (2)$$

$$CH_2BrCHBrOC_2H_5 + CH_3MgCl \longrightarrow CH_2BrCH(OC_2H_5)CH_3 + MgClBr \quad (3)$$

$$CH_2BrCH(OC_2H_5)CH_3 + KOH \longrightarrow CH_2=C(OC_2H_5)CH_3 + KBr + H_2O \quad (4)$$

(1) Presented before the Organic Division at the New York meeting, April, 1935.

(2) Leendertse, Tulleners and Waterman, Rec. trav. chim., 52, 515 (1933).

(3) Norris and Joubert, THIS JOURNAL, 49, 873 (1927).

(4) Bourguel and Piaux, Bull. soc. chim., 51, 1041 (1932).

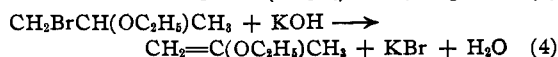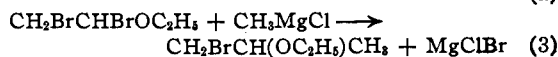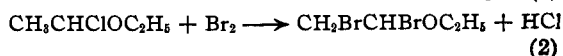(5) Church, Whitmore and McGrew, THIS JOURNAL, 56, 176 (1934).

(6) Wassilijeff, Chem. Zentr., 70, 1, 775 (1899); J. Russ. Phys.-Chem. Ges., 30, 993 (1897).

(7) Michael and Zeidler, Ann., 385, 251 (1911).
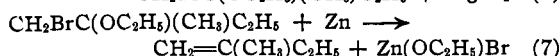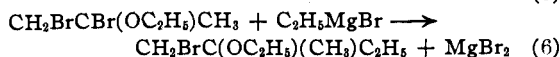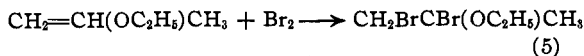
(8) Le Bel, Bull. soc. chim., [2] 25, 546 (1870).

(9) Walker and Wood, J. Chem. Soc., 89, I, 604 (1906).

(10) Master's theses and Honor papers, Mount Holyoke College: A. Jackson, 1929; R. Comroe, 1931; E. Burkey, 1933; M. Adams, C. Monod, 1935.

(11) Boord and co-workers, THIS JOURNAL, 1930, to date.

$$CH_2{=}CH(OC_2H_5)CH_3 + Br_2 \longrightarrow CH_2BrCBr(OC_2H_5)CH_3 \quad (5)$$

$$CH_2BrCBr(OC_2H_5)CH_3 + C_2H_5MgBr \longrightarrow$$
$$CH_2BrC(OC_2H_5)(CH_3)C_2H_5 + MgBr_2 \quad (6)$$

$$CH_2BrC(OC_2H_5)(CH_3)C_2H_5 + Zn \longrightarrow$$
$$CH_2{=}C(CH_3)C_2H_5 + Zn(OC_2H_5)Br \quad (7)$$

Since certain of the intermediates obtained in this research were probably in a purer form than those hitherto known, the values of their physical constants are given in Table I, and their ultraviolet absorption curves in Fig. 1. The physical constants for 2-methylbutene-1, together with those for all the pentenes which have been investigated in this Laboratory and Norris and Reuter's[12] data for isopropylethylene, are summarized in Table II. It was found that 2-methylbutene-1 does not form peroxides readily. After several months this hydrocarbon gave no peroxide test and in this respect behaves more like pentene-1 than pentene-2 or trimethylethylene, both of which form peroxides very readily.
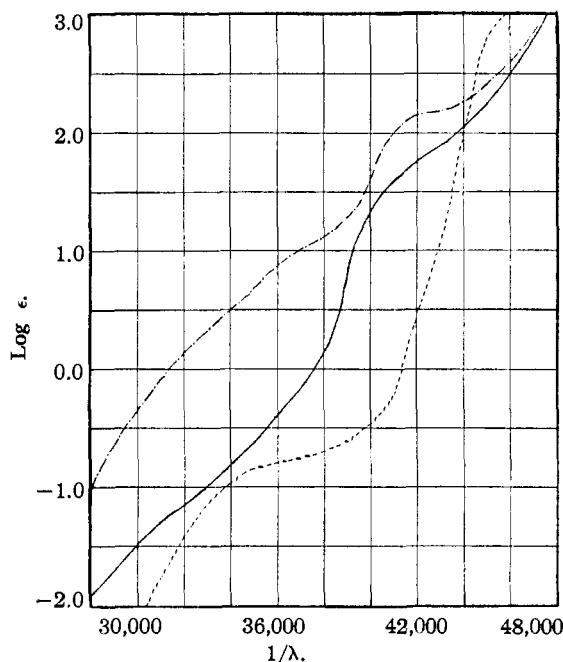

Fig. 1.—————, 1-Bromo-2-ethoxypropane; — — —, 2-ethoxypropene; —·—, 1-bromo-2-ethoxy-2-methylbutane.

The ultraviolet absorption curves for the four pentenes which have been investigated in this Laboratory are given in Fig. 2 and it will be noted that although the curves of the four hydrocarbons are somewhat similar, there are certain distinguishing characteristics which differentiate the various isomers. All of the pentenes show a step-

out in the region 42,000–45,000 cm.⁻¹; the intensity of this band varies somewhat with the different isomers but the marked differences in absorption are shown in the position of the step-out in the longer wave region. The position of this band of low intensity is characteristic of the number and to a less extent the arrangement of alkyl groups around the double bond. The similarity in absorption between pentene-2 and 2-methylbutene-1 is of particular interest but detailed discussion of these curves will be given in a later paper from this Laboratory together with the report of the results of absorption spectra measurements of these hydrocarbons in the Schumann region.
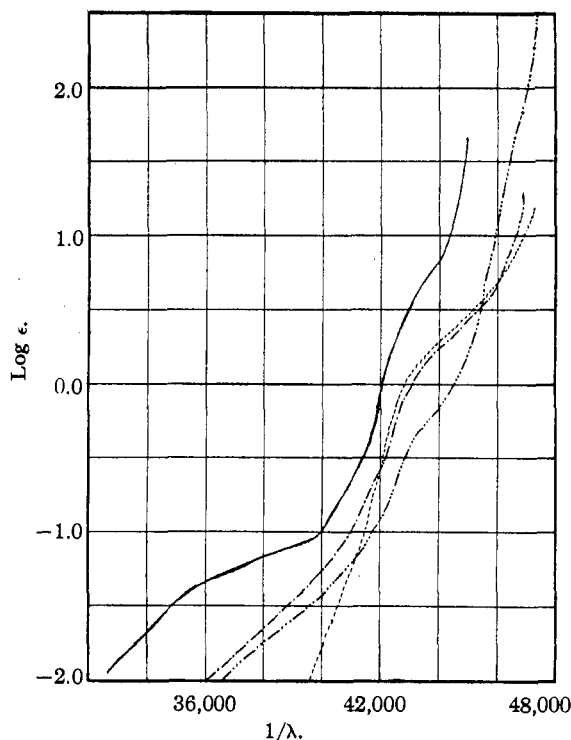

Fig. 2.— ———, Trimethylethylene; — — —, 1-pentene; —·—, 2-pentene; —···—, 2-methylbutene-1.

The Raman spectrum of 2-methylbutene-1 has been determined and is reported in the paper following.[13]

Experimental

α-Chloroethyl Ethyl Ether and 1,2-Dibromoethyl Ethyl Ether.—Dry hydrogen chloride in slight excess was passed into an equimolecular mixture of acetaldehyde and absolute ethyl alcohol. The average yield of the α-chloro ether from thirty-four preparations (2 moles each) was 78%; the colorless product was immediately brominated with an average yield of 92% of 1,2-dibromoethyl ethyl

(12) Norris and Reuter, THIS JOURNAL, 49, 2624 (1927).

(13) Thompson and Sherrill, ibid., 58, 745 (1936).

Compound	B. p., °C.	Press., mm.	$n^{20}D$	d^{20}_4	Mol. ref. Calcd.	Found
1-Bromo-2-ethoxypropane	28.6– 28.8	10	1.4422	1.2754	34.70	34.67
	138.0–138.1	760				
2-Ethoxypropene	61.2– 61.8	760	1.3913	0.7713	26.46	26.54
1-Bromo-2-ethoxy-2-methylbutane	53.4– 53.6	9.5	1.4514	1.2040	43.93	43.67

TABLE II
PHYSICAL CONSTANTS OF THE PENTENES

Compound	B. p., °C., 760 mm.	$n^{20}D$	d^{20}_4	Mol. ref. Calcd. 24.82
Pentene-1	30.10 ± 0.05	1.3710	0.6410	24.78
Pentene-2 (symmetrical methylethylethylene)	36.40 ± 0.05	1.3797	.6505	24.90
2-Methylbutene-1 (unsymmetrical methylethylethylene)	31.05 ± 0.05	1.3777	.6504	24.77
3-Methylbutene-1[12] (isopropylethylene)	20.1 ± 0.05	1.3675 (15°)	.6320 (15°)	24.90
2-Methylbutene-2 (trimethylethylene)	38.42 ± 0.05	1.3878	.6620	24.91

ether. The dried product, a total of 11,442 g. from all preparations, was used without further purification in the Grignard synthesis.

1-Bromo-2-ethoxypropane.—The Grignard reagent, methylmagnesium chloride (90% yield), was prepared by passing methyl chloride into 1 liter of anhydrous ethyl ether containing magnesium turnings (2.5 moles). To this excess of reagent at 0° was added the 1,2-dibromoethyl ethyl ether (1.4 moles) diluted with an equal volume of ether. The total weight of crude 1-bromo-2-ethoxypropane was 4735 g. (57%). Usually the product was pale yellow but in a few cases it was very dark and was then steam distilled before further purification. Distillation at atmospheric pressure was not satisfactory but excellent results were obtained when it was distilled from a few pellets of sodium hydroxide at diminished pressure. After one distillation the density was d^{20}_{20} 1.2705 (d^{20}_4 1.2679), which checks that reported by Swallen and Boord.[11] Further purification gave a product (3415 g., 42%) whose physical constants are given in Table I.

2-Ethoxypropene.—1-Bromo-2-ethoxypropane (2 moles) was heated with a large excess of potassium hydroxide[14] in a copper flask fitted with a brass stirrer, a mercury seal and a short fractionating column. Distillation of the unsaturated ether began after heating the reaction mixture to 110–115° for one hour and continued with gradual increase of temperature to about 160°. The temperature at the head of the column was 57–60°. The yield of crude product was 90%. This was purified by distillation from potassium hydroxide using a Vigreux column. The total weight of purified 2-ethoxypropene was 1123 g. (64%).

1,2-Dibromo-2-ethoxypropane.—2-Ethoxypropene (1 mole) dissolved in 500 cc. of anhydrous ethyl ether was treated with bromine (1 mole), the reaction flask being kept at −10° and the contents stirred continuously. The dibromo ether was not isolated.

1-Bromo-2-ethoxy-2-methylbutane.—The ether solution of 1,2-dibromo-2-ethoxypropane, pale yellow in color, was added directly to well-cooled ethylmagnesium bromide (25% excess). The crude yield of 1-bromo-2-ethoxy-2-methylbutane, orange red in color, was 65%. This was purified by steam distillation and then by distillation under

diminished pressure through a Vigreux column, giving 673 g. (27%) of a colorless compound, b. p. 56.4–57.0° at 13 mm., $n^{20}D$ 1.4508, which was used for the preparation of the 2-methylbutene-1. There are no recorded data for this compound so a portion was redistilled until constant density and index were obtained.

2-Methylbutene-1.—The 1-bromo-2-ethoxy-2-methyl-butane (1.67 moles) was added to a hot suspension (70°) of 100 g. of zinc dust and 15 g. of activated zinc (zinc–copper) in 500 cc. of 95% alcohol. The hydrocarbon distilled over (32–35°) at a rate corresponding to the bromo ether addition. More zinc (200 g.) was added in two portions as the reaction progressed. The total weight of hydrocarbon ($n^{20}D$ 1.3790) was 176 g. (74%). To prevent possible peroxide formation all subsequent treatment was carried out in nitrogen filled apparatus, nitrogen also being passed through the water used in washing and the alcohol solvent. A mixture of 2-methylbutene-1 and an equal volume of absolute methyl alcohol was distilled through a Crismer column (150 × 1.5 cm., 102 turns in the spiral). The azeotropic mixture distilled constantly at 27.5 ± 0.05° at 760 mm., for eight hours. The hydrocarbon, washed free from alcohol and dried over calcium oxide had an index $n^{20}D$ 1.3783. The 2-methylbutene-1 was distilled twice through a Fenske column,[15] (35 × 1.5 cm., 1 turn 4 mm. glass helices) the reflux ratio being 1:30; the time required for the total distillate of 149 g. was seventeen hours. The hydrocarbon distilled constantly at 31.05 ± 0.05° at 760 mm., the first, middle and last fractions of both distillations having the same physical constants. The refractive indices of the distillate and the residue were identical $n^{20}D$ 1.3783.

Bromine Addition Product.—The 1,2-dibromo-2-methyl-butane was prepared by adding the theoretical amount of bromine in carbon tetrachloride solution to a well-cooled solution of the 2-methylbutene-1 in the same solvent. The dibromide was distilled *in vacuo* and the physical properties of the compound obtained are as follows: b. p. 47.4–48.0° at 8.5–9.0 mm.; $n^{20}D$ 1.5088; d^{20}_4 1.6711. The only recorded data are those of Wassiljeff.[6]

Absorption Spectra.—Ultraviolet absorption spectra measurements were made on samples of 2-methylbutene-1

(14) Lauer and Spielman, THIS JOURNAL, **53**, 1552 (1931).

(15) Fenske, *Ind. Eng. Chem.*, **26**, 1169 (1934); **24**, 408, 482, 814 (1932).

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.

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

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 de-

hydrating 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

(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).