





In general those methods involving pyrolysis such as the dehydration of an alcohol or the decomposition of a quaternary ammonium salt are likely to cause a migration of the double bond. In such a case the olefin obtained may not have the structure indicated by the synthesis. Boiling an unsaturated compound with alcoholic potash is also a well-known method for shifting the position of a double bond.<sup>8</sup> This fact leads one to accept, with some reservation, the structure of those olefins prepared by many of the methods commonly used.

A second source of confusion in the literature of the hexenes arises from the fact that several of them were first prepared by the dehydration of pinacolin alcohol. During the early work the structure of pinacolin alcohol itself was in doubt<sup>9</sup> and later it was shown to be a mixture or at least to yield a mixture of bromides,<sup>10</sup> giving rise to a number of hexenes.

These considerations lead one to place the greatest reliance on those methods requiring only low temperatures such as the action of alkylmagnesium halides upon allyl bromide<sup>11</sup> or of metallic zinc upon the corresponding dibromide in alcoholic solution.<sup>12</sup>

The present method has an added advantage in that the nucleus is built up by definitely known steps, the double bond being introduced in the final step at a temperature which need not exceed the boiling point of propyl alcohol.

### Physical Properties and Structure

In previous communications we formulated certain tentative rules relating the boiling point of an olefin to its structure. It will be observed from Table I that 1-hexene boils lower than 2-hexene and 4-methyl-1-pentene lower than 4-methyl-2-pentene. Indeed 4-methyl-1-pentene boils lower than either of the two forms of 4-methyl-2-pentene. These facts support the previous conclusion that *α-olefins boil lower than β-olefins*.

A further inspection of Table I shows an interesting sequence in the physical constants of the hexenes of type I. *Tert.*-butylethylene (3,3-dimethyl-1-hexene) boils lower than either *sec.*-butylethylene (3-methyl-1-pentene) or isobutylethylene (4-methyl-1-pentene) and these in turn lower than *n*-butylethylene (1-hexene). Among the hexenes of type II, both forms of 4-methyl-2-pentene boil lower than 2-hexene and among

<sup>8</sup> Eykman, *Ber.*, **23**, 855 (1890); Ciamician and Silber, *ibid.*, **23**, 1159, 1164 (1890); Thiele and Henle, *Ann.*, **347**, 310 (1906).

<sup>9</sup> Couturier, *Ann. chim. phys.*, [6] **26**, 460 (1892).

<sup>10</sup> Delacre, *Bull. soc. chim.*, [3] **35**, 811 (1906); Zelinsky and Telikow, *Ber.*, **34**, 3249 (1901).

<sup>11</sup> (a) Brooks and Humphrey, *THIS JOURNAL*, **40**, 829 (1918); (b) Kirmann, *Bull. soc. chim.*, [4] **39**, 990 (1926); (c) Mlle. v. Risseghem, *Bull. soc. chim. Belg.*, **35**, 345 (1926).

<sup>12</sup> (a) Gladstone and Tribe, *Ber.*, **7**, 364 (1874); *J. Chem. Soc.*, **21**, 306 (1878); (b) Lespieau and Wiemann, *Bull. soc. chim.*, **45**, 627 (1929).

TABLE I  
 THE PHYSICAL CONSTANTS AND CONSTITUTION OF THE HEXENES

Structure	Type	B. p., °C. (760 mm.)	$d_4^{20}$	$n_D^{20}$	M. R. calcd.	M. R. obs.	Investigator
<chem>C=C-C-C-C-C</chem>	I	63.4-63.7 63.35 ± 0.05 64.5-65	0.6732 .67875 <sup>15</sup> .684 <sup>14</sup>	1.3858 1.3885 <sup>15</sup> <sub>D</sub> 1.393 <sup>14</sup> <sub>D</sub>	29.44 29.27 29.33	29.33 29.27 <sub>H</sub> ± 29.23	Present paper v. Risseghem <sup>a</sup> Bourguel <sup>b</sup>
<chem>C=C-C-C-C</chem>   C	I	53.6-54.0	.6700	1.3835	29.44	29.31	Present paper
<chem>C=C-C-C-C</chem>   C	I	53.6-53.9	.6646	1.3825	29.44	29.48	Present paper
<chem>C=C-C-C</chem>   C   C	I	41.2	.6549 <sup>18</sup> <sub>4</sub>	1.3766 <sup>18</sup> <sub>D</sub>	29.33	29.53	Fomin-Sochanski <sup>c</sup>
<chem>C-C=C-C-C-C</chem>	II	67.9-68.1 68.0-68.2 67.7-68.1	.6813 .6863 <sup>14</sup> .66888	1.3928 1.3981 <sup>18</sup> <sub>D</sub> 1.38319	29.44 29.27 <sub>H</sub> ± 29.325	29.45 29.42 29.307	Present paper v. Risseghem <sup>d</sup> v. Beresteyn <sup>e</sup>
<chem>C-C=C-C-C</chem> (H.B.)   C	II	57.7-58.5 57-58.5	.6709 .6706	1.3885 1.3883	29.44 29.32	29.61 29.58	Present paper Gorsky <sup>f</sup>
<chem>C-C=C-C-C</chem> (L.B.)   C	II	54.2-55.2	.6702	1.3881	29.44	29.61	Present paper
<chem>C-C-C=C-C-C</chem>	II	66.6-67.0 64.0	.6816 .6807 <sup>19</sup>	1.3942 1.394 <sup>19</sup> <sub>D</sub>	29.44 29.44	29.53 29.52	Present paper Lesp.-Wiem. <sup>g</sup>
<chem>C=C-C-C-C</chem>   C	III	61.5-62.0 64-66	.6817 ...	1.3921 ...	29.44 ...	29.38 ...	Present paper Brooks-Humph. <sup>h</sup>
<chem>C=C-C-C</chem>   C   C	III	56.0-56.5 55.0-57.5	.6803 ...	1.3995 ...	29.44 ...	29.33 ...	Present paper
<chem>C=C-C-C</chem>   C   C	III	66.2-66.7 67-68	.6914 .69403	1.3990 1.40276	29.44 29.44	29.41 29.55	Present paper Kon <sup>i</sup>
<chem>C-C=C-C-C</chem> (H.B.)   C	IV	67.6-68.2 69.9-70.2	.6956 .7022 <sup>5</sup> <sub>4</sub>	1.4002 1.4072 <sup>5</sup> <sub>D</sub>	29.44 ...	29.32 29.61	Paul Flory <sup>m</sup> v. Risseghem <sup>i</sup>
<chem>C-C=C-C-C</chem> (L.B.)   C	IV	65.7-66.2 65.1-65.7	.6940 .7220 <sup>15</sup> <sub>4</sub>	1.3994 1.3997 <sup>15</sup> <sub>D</sub>	29.44	29.34	Paul Flory <sup>m</sup> v. Risseghem <sup>i</sup>
<chem>C-C=C-C-C</chem>   C	IV	67.2-67.5 66.7-67.1	.6904 .69145 <sup>5</sup> <sub>4</sub>	1.4005 1.4028 <sup>5</sup> <sub>D</sub>	29.44 29.44	29.56 29.674	Present paper v. Risseghem <sup>k</sup>
<chem>C-C=C-C</chem>   C   C	V	73-74	.7077	1.4248	29.44	29.32	v. Risseghem <sup>l</sup>

<sup>a</sup> Ref. 11 c. <sup>b</sup> Bourguel, *Bull. soc. chim.*, **41**, 1475 (1927). <sup>c</sup> Fomin and Sochanski, *Ber.*, **46**, 246 (1931). <sup>d</sup> Ref. 11 c, p. 333. <sup>e</sup> v. Beresteyn, *Bull. soc. chim. Belg.*, **25**, 293 (1911). <sup>f</sup> Gorsky, *J. Russ. Phys.-Chem. Soc.*, **42**, 1356 (1910). <sup>g</sup> Ref. 12 b. <sup>h</sup> Ref. 11 a, p. 831. <sup>i</sup> Kon, *J. Chem. Soc.*, **119**, 810 (1921). <sup>j</sup> v. Risseghem *Bull. soc. chim. Belg.*, **31**, 213 (1922). <sup>k</sup> v. Risseghem, *ibid.*, **32**, 144 (1923). <sup>l</sup> v. Risseghem, *ibid.*, **30**, 9 (1921). <sup>m</sup> Flory and Boord, incomplete and unpublished work now being done in this Laboratory.

those of type III, 2,3-dimethyl-1-butene boils lower than 2-methyl-1-pentene. These facts lead to the conclusion that *branching in an alkyl group attached to an unsaturated carbon atom of an olefin tends to lower the boiling temperature.*

The above conclusion seems to stand in direct contradiction to a gen-

eralization made many years ago by Pawlow.<sup>13</sup> This author, having in mind the boiling points of tetramethylethylene and of the two dimethylethylethylenes, was led to observe that: "In the saturated compounds the accumulation of methyl groups in most cases lowers the boiling point, in hydrocarbons of the ethylene series, on the other hand, the same condition seems to be able to raise the boiling temperature." Pawlow failed to restrict his generalization to those olefins in which the methyl groups are bound directly to the unsaturated carbon atoms. Table I shows tetramethylethylene (2,3-dimethyl-2-butene) to be the highest boiling hexene. All the hexenes of type IV, having two methyl groups attached to unsaturated carbon, boil above 65°. The other hexenes boiling above this temperature include 2-hexene, 3-hexene and *unsym.*-diethylethylene (2-ethyl-1-butene). These facts stand in agreement with Pawlow's generalization, which may now be restated in a modified form: *the accumulation of methyl groups on the unsaturated carbon atoms of an olefin tends to raise the boiling point.* This conclusion seems to be supported by the fact that  $\beta$ -olefins always boil distinctly higher than  $\alpha$ -olefins while (in so far as data are available)  $\beta$ -olefins also boil higher than  $\gamma$ -olefins.

Holding in mind both of the above conclusions one is tempted to make the broader generalization: *The more deeply the point of unsaturation is buried within the molecular structure the higher the boiling point; or, conversely: the more exposed the point of unsaturation the lower the boiling point.* The data available are probably not sufficient to justify so broad a generalization but as was previously pointed out *tert.*-butylethylene (3,3-dimethyl-2-butene) having both a highly branched alkyl group and an exposed double bond is the lowest boiling of all the hexenes; while tetramethylethylene (2,3-dimethylethylene) with its double bond completely submerged in the molecular structure is the highest boiling hexene. In the light of the above generalization it is interesting to observe that 2-methyl-1-pentene boils lower than 1-hexene and it is easily conceivable that in the average molecular configuration of the former (A) the point of unsaturation may be



more exposed than in the latter (B). It is also of interest to note that the boiling points of *sym.*-diethylethylene (3-hexene) and *unsym.*-diethylethylene (2-ethyl-1-butene) lie very close together.

In general the densities and the refractive indices of the hexenes follow the boiling points. *Tert.*-butylethylene is the lightest and the least refractive, while tetramethylethylene is the heaviest and has the highest re-

<sup>13</sup> Pawlow, *Ann.*, **196**, 126 (1879).

fractive power. It will be observed that for the hexenes of type I and for the  $\beta$ -hexenes of type II the density and the refractivity follow exactly the same order as the boiling point. For those of types III and IV the parallelism is not so marked but in general a high boiling point indicates high density and high refractive index.

*Cis-Trans Isomerism.*—Two isomeric forms have been found for both 3-methyl-2-pentene and 4-methyl-2-pentene. The former case has been carefully studied by Mlle. v. Risseghem,<sup>14</sup> using a large quantity of material. The low-boiling isomer was of doubtful purity since its density was unusually high and its molecular refractivity correspondingly low.

The data attributed to Flory and one of us on this compound are taken from incomplete and unpublished work now being done in this Laboratory on the application of the  $\beta$ -bromo ether synthesis to the olefins of type IV. The low-boiling isomer, as obtained by us, seems to correspond closely with that given by Mlle. v. Risseghem. The density and molecular refractivity are even more acceptable. Our high-boiling isomer does not correspond to the main fraction obtained by this investigator, but rather to a small intermediate fraction indicated in her distillation data. The data must be regarded as tentative and subject to verification as the investigation develops.

4-Methyl-2-pentene is described for the first time in the present paper. The amount of this hydrocarbon available was not sufficient for a completely detailed study and the purity of the low-boiling isomer was not wholly satisfactory. Its boiling point range covered an entire degree. The partition of each of these two hexenes into two isomeric forms is sufficiently definite, however, as to leave no possible doubt as to their separate existence.

The criteria which have been used for determining the true identity of the *cis* and *trans* forms in such a case have led to contradictory results. Wislicenus and his co-workers<sup>15</sup> regard the low-boiling isomer of 2-butene as the *cis* form. Pfeiffer<sup>16</sup> on the other hand believed the low-boiling to be the *trans* form, and Lucas and his co-workers<sup>17</sup> have chosen to agree with this point of view. Van de Walle and Henne,<sup>18</sup> working with the halogen substituted ethylenes and following the principles laid down by Michael,<sup>19</sup> found that the *trans* form was usually the low-boiling isomer. 1,2-Diodoethylene was the only exception.

If it is true that that isomer having its double bond most deeply buried in

<sup>14</sup> Van Risseghem, *Bull. soc. chim. Belg.*, **31**, 213 (1922).

<sup>15</sup> Wislicenus, Talbot, Henze and Schmidt, *Ann.*, **313**, 207-250 (1900).

<sup>16</sup> Pfeiffer, *Z. physik. Chem.*, **48**, 58 (1904).

<sup>17</sup> Young, Dillon and Lucas, *THIS JOURNAL*, **51**, 2528 (1929).

<sup>18</sup> Van de Walle and Henne, *Bull. acad. roy. Belg.*, 360-374 (1925).

<sup>19</sup> Michael, *J. prakt. Chem.*, **46**, 222 (1892); **52**, 352 (1895).

the molecular structure has the highest boiling point, then one would expect this to be the *trans* isomer. The difference in boiling point between the two isomeric forms of 3-methyl-2-pentene is 4.5–4.8° (v. Risseghem) and of 4-methyl-2-pentene is 3.0–3.4°.

Should the above point of view prove to be justifiable, one may find here a possible explanation for the apparent non-existence of *cis-trans* isomerism in the case of 2-hexene and 3-hexene. Since in such a case the double bond would be about equally exposed in the *cis* and the *trans* configurations the boiling points would lie very close together, requiring more refined fractionation than has been possible up to the present time.

**Criteria of Purity.**—In a critical study of the simple olefins one finds the usual criteria for purity of doubtful value. Many olefins are readily subject to isomerization and polymerization. All of them tend to form azeotropic mixtures. The products obtained usually boil over a range of temperatures. In the present investigation, with a single exception, the purified products have been obtained with a boiling range of less than 0.5°. Since all olefins have the same composition, ultimate analysis does not reveal impurities due to admixture with isomers or polymers.

A comparison of the observed with the calculated molecular refractivities is also frequently used as an index of purity. It should be pointed out that while this method would reveal any considerable admixture with polymer it would be wholly ineffectual in a mixture of isomers. Columns five and six (Table I) show the observed and calculated refractivities of the hexenes. The measurements are for the sodium D-line except as otherwise indicated. The experimentally determined values, in general, are in better agreement with 29.44, the calculated value based on Eisenlohr's constants, than with 29.325, the value when Brühl's constants are used. It has long been known that many unsaturated compounds show anomalous molecular refractivity. This anomaly is especially characteristic of compounds containing conjugated double bonds. Since the physical constants of the hexenes vary so widely with the position of the double bond in the molecular structure, one is led to doubt whether the double bond should be given the same weighting in all types of simple olefins.

### Experimental Part

**$\alpha$ -Chloro Ethers.**—The  $\alpha$ -chloro ethers were prepared by the method previously described.  $\alpha$ -Chloroethyl-<sup>1a</sup> and  $\alpha$ -chloro-*n*-propyl ethyl ether<sup>1b</sup> were obtained in 89 and 70% yields, respectively.

$\alpha$ -Chloro-isobutyl ethyl ether,  $(\text{CH}_3)_2\text{CHCHClOC}_2\text{H}_5$ , which it seems has not been previously described, was obtained in 90% (crude) yield, b. p. 43° (24 mm.),  $d_4^{20}$  0.9316,  $n_D^{20}$  1.4130, M. R. calcd., 36.42, M. R. observed, 36.46.

*Anal.* Calcd. for  $\text{C}_6\text{H}_{12}\text{OCl}$ : Cl, 25.97. Found: Cl, 25.09.

**$\alpha,\beta$ -Dibromo Ethers.**—The dibromo ethers used in the present investigation were prepared by three different methods.  $\alpha,\beta$ -Dibromoethyl- and  $\alpha,\beta$ -dibromo-*n*-propyl

ethyl ethers, prepared as described in previous communications,<sup>1b,c</sup> were obtained in 95 and 94% (crude) yields, respectively.

$\alpha,\beta$ -Dibromo-isobutyl-ethyl ether,  $(\text{CH}_3)_2\text{CBrCHBrOC}_2\text{H}_5$ , was prepared by an analogous method in 92% yield, b. p. 88–89° (22 mm.),  $d_4^{20}$  1.5671,  $n_D^{20}$  1.4450, M. R. calcd. 48.08, M. R. observed 44.20.

*Anal.* Calcd. for  $\text{C}_6\text{H}_{12}\text{OBr}_2$ : Br, 61.49. Found: Br, 60.29.

$\alpha,\beta$ -Dibromo-*m*-butyl methyl ether,  $\text{CH}_3\text{CH}_2\text{CHBrCHBrOCH}_3$ , was prepared by a modification of the method of Späth and Göhring.<sup>20</sup> One mole of *n*-butyraldehyde was cooled and mixed with an excess of cold methyl alcohol. This solution was brominated at 0° using one molar quantity of bromine. The mixture was saturated with hydrogen bromide and the lower layer of  $\alpha,\beta$ -dibromo-*n*-butyl methyl ether was separated. The crude product was placed over anhydrous calcium chloride and the volatile impurities removed under diminished pressure. The crude dibromo ether was used without further purification.

The third method of preparing  $\alpha,\beta$ -dibromo ethers consisted in adding bromine to the  $\alpha,\beta$ -unsaturated ethers of the type described by Lauer and Spielman.<sup>4</sup> These authors have shown that the  $\beta$ -bromo ethers, described by Swallen and one of us, react with powdered potassium hydroxide with the loss of hydrogen bromide, forming the unsaturated ethers indicated above.

The required  $\beta$ -ethoxy-*n*-propyl bromide and  $\beta$ -ethoxy-*n*-butyl bromide were prepared as previously described in yields of 71 and 75%, respectively. Each of these  $\beta$ -bromo ethers was placed in a three-necked iron flask<sup>21</sup> and mixed with twice its weight of finely powdered anhydrous potassium hydroxide. The flask was provided with an iron stirrer having a mercury seal and thirty or forty one-half inch iron balls (ball bearings) were also added to aid in breaking up the salt incrustations as the reaction proceeded. The generator was provided with a Hempel distilling column which in turn was attached to an efflux condenser and a thermometer so arranged as to indicate the boiling point of the distillate. The flask was jacketed with asbestos paper and heated over an electric hot-plate. The effluence of the unsaturated ether was practically completed in three to four hours. The temperature was then raised to drive over the last portions. The receiver was protected from the moisture of the air by a calcium chloride tube and the product collected over a small amount of solid potassium hydroxide. In spite of all precautions the product always contained a small amount of the corresponding ketone and some unchanged  $\beta$ -bromo ether. It was separated from the latter by fractionation. No attempt was made to remove the trace of ketone.

By the above procedure  $\beta$ -ethoxy-*n*-propyl bromide was made to yield 83% of 2-ethoxypropene,<sup>4</sup> b. p. 61–63° (748 mm.),  $d_4^{20}$  0.7712,  $n_D^{20}$  1.3915, M. R. calcd. 26.44, M. R. observed 26.55, and  $\beta$ -ethoxy-*n*-butyl bromide to yield 70% of 2-ethoxy-1-butene,<sup>22</sup> b. p. 84–87° (7.45 mm.),  $d_4^{20}$  0.7848,  $n_D^{20}$  1.4018, M. R. calcd. 31.16, M. R. observed 31.03. These values agree well with those previously recorded.

One mole of the 2-ethoxy olefin was dissolved in 500 cc. of anhydrous ether, the solution cooled to –10° and one mole of pure dry bromine added slowly. The mixture was stirred during the bromination, the product being protected from the moisture by a calcium chloride tube. If the temperature is maintained below –5° the product will be quite colorless. No attempt was made to isolate the dibromo ether but the ethereal solution was converted at once by condensation with the appropriate Grignard reagent

<sup>20</sup> Späth and Göhring, *Monatsh.*, **41**, 319 (1920).

<sup>21</sup> This flask was kindly loaned to us by Dr. G. Bryant Bachman of this Department. It gave excellent service.

<sup>22</sup> Faworski. *J. prakt. Chem.*, [2] **37**, 533 (1888).



into the desired  $\beta$ -bromo ether. In this manner 2-ethoxypropene and 2-ethoxy-1-butene were converted into 1,2-dibromo-2-ethoxypropane and 1,2-dibromo-2-ethoxy-*n*-butane, respectively.

$\beta$ -Bromo- $\alpha$ -ethoxyhexanes.—The Grignard solutions used in the present investigation were prepared and evaluated by the method described by Gilman and his co-workers.<sup>23</sup> The condensations to form the  $\beta$ -bromo ethers were carried out by the procedure indicated by Shoemaker and one of us. It has been observed in the present work that a 10 to 30% excess of Grignard reagent is desirable. Furthermore the best results are obtained by stirring the reaction mixture from ten to fifteen hours after the addition is completed. The condensations are best made in dilute solution. Table II gives the physical constants and analyses of the ten  $\beta$ -bromo- $\alpha$ -ethoxyhexanes used in the present investigation.

TABLE II  
 $\beta$ -BROMO- $\alpha$ -ETHOXYHEXANES

Name	B. p., °C. (mm.)	$d_4^{20}$	$n_D^{20}$	M. R. obs. Calcd., 48.55	Analysis, Br. % Calcd.	Br. % Found
1-Bromo-2-ethoxyhexane <sup>a</sup>	86.5 (19)	1.1488	1.4485	48.71	38.23	37.99
1-Bromo-2-ethoxy-4-methylpentane <sup>b</sup>	85.0 (25)	1.1468	1.4455	48.50	38.23	38.25
1-Bromo-2-ethoxy-3-methylpentane	74.75 (13)	1.1682	1.4503	48.08	38.23	38.28
2-Bromo-3-ethoxyhexane	73.0 (12)	1.1455	1.4474	48.71	38.23	38.22
2-Bromo-3-ethoxy-3-methylpentane	79.5 (25)	1.1377	1.4458	49.13	38.23	38.12
4-Bromo-3-methoxyhexane	65-66 (12)	1.2378	1.4495	42.32	40.97	40.76
1-Bromo-2-ethoxy-2-methylpentane	81-82 (19)	1.1706	1.4532	48.29	38.23	38.20
1-Bromo-2-ethoxy-2,3-dimethylbutane	78-79 (15)	1.1671	1.4560	48.71	38.23	38.12
1-Bromo-2-ethoxy-2-ethylbutane	79-81 (17)	1.1758	1.4548	48.29	38.23	37.97
2-Bromo-3-ethoxy-2-methylpentane <sup>c</sup>	65-67 (20)	0.9557	1.4376	...	38.23	

<sup>a</sup> Swallen and Boord, *THIS JOURNAL*, **52**, 655 (1930). <sup>b</sup> Dykstra, Lewis and Boord, *ibid.*, **52**, 3401 (1930). <sup>c</sup> This compound was not pure and did not yield to purification.

**Preparation of the Hexenes.**—The  $\beta$ -bromo ethers described above were converted into the corresponding hexenes by the action of zinc dust on the alcoholic solution as previously indicated. From 50 to 100 g. of the bromoethoxyhexane (or in one case bromomethoxyhexane) was dissolved in 125 to 175 cc. of *n*-propyl alcohol and 35 to 75 grams of zinc dust added. The mixture was refluxed at the incipient boiling temperature for ten to fifteen hours. The contents of the flask were then submitted to distillation. Distillation began near the boiling point of the azeotropic mixture of the alcohol and olefin and gradually rose to that of the pure alcohol. By the time the latter temperature had been reached all the olefin had distilled. The distillate was diluted with twice its volume of cold water and the upper olefinic layer separated. The hexene was washed four or five times with an equal volume of cold water and dried over granular calcium chloride. The olefin was then distilled over metallic sodium to remove the last traces of alcohol and water.

Table III shows the starting materials and the yield obtained in each step of the synthesis. The last column of this table also shows the "over all" yield of hexene based on the aldehyde. The boiling points, densities, refractive indices and molecular refraactivities of the hexenes prepared in the present investigation are shown in Table I.

**Dibromohexanes.**—For the purpose of analysis and characterization, each of the above hexenes was converted into the corresponding dibromohexane. Ten grams of the olefin was dissolved in 50 cc. of chloroform and the solution cooled to 0°. An equivalent amount of pure dry bromine also dissolved in 50 cc. of chloroform was slowly added. The temperature of the reaction mixture was maintained below 5°, and the reaction

<sup>23</sup> (a) Gilman, Zoellner and Dickey, *THIS JOURNAL*, **51**, 1576 (1929); (b) Gilman, Wilkinson, Fishel and Meyers, *ibid.*, **45**, 150 (1923).

TABLE III  
 YIELD VALUES BY STEPS IN THE HEXENE SYNTHESSES

Hexene	Aldehyde	R—Mg—Br	I α-Chloro ether	II Di- bromo ether	III β- Bromo ether	IV Olefin	Un- satd. ether	Total yield on aldehyde
1-Hexene	Acet-	<i>n</i> -Butyl	89	95	78	78	..	51.4
4-Methyl-1-pentene	Acet-	Isobutyl	89	95	48	57	..	23.1
3-Methyl-1-pentene	Acet-	<i>s</i> -Butyl	89	95	30	72	..	18.3
2-Hexene	Propion-	<i>n</i> -Propyl	70	94	60	75	..	29.6
4-Methyl-2-pentene	Propion-	Isopropyl	70	94	55	70 <sup>a</sup>	..	25.35
3-Hexene	<i>n</i> -Butyl-	Ethyl	..	..	68	85	..	..
2-Methyl-1-pentene	Acet-	Methyl	89	95	71	..	83	..
		<i>n</i> -Propyl	(2-ethoxypropene)	?	55	65	..	17.8
2,3-Dimethyl-1-butene	Acet-	Methyl	89	95	71	..	83	..
		Isopropyl	(2-ethoxypropene)	?	48	70	..	16.7
2-Ethyl-1-butene	Acet-	Ethyl	89	95	75	..	70	..
		Ethyl	(2-ethoxy-1-butene)	?	55	58	..	14.2
2-Methyl-2-pentene	Isobuty-	Ethyl	90	92	49	40	..	16.2

<sup>a</sup> This number represents the total yield including both forms. Of this amount fifty parts were obtained as the high boiling form and twenty parts as the low boiling form. This is equivalent to a total yield on the basis of the aldehyde and of 18.1 and 7.25% of the high and low boiling forms, respectively.

carried out in diffused light. The chloroform was distilled off and the dibromide distilled under diminished pressure. The yields were approximately quantitative.

The physical constants and analyses of the dibromohexanes are shown in Table IV.

 TABLE IV  
 DIBROMOHEXANES

Name	B. p., °C. (mm.)	$d_4^{20}$	$n_D^{20}$	M. R. obs. Calcd. 45.44	Br. % found Calcd. 65.53
1,2-Dibromohexane <sup>a,b</sup>	89–90 (18)	1.5774	1.5024	45.62	65.59
1,2-Dibromo-3-methylpentane	99 (30)	1.6016	1.5060	44.90	65.42
1,2-Dibromo-4-methylpentane <sup>1b</sup>	87 (21)	1.5689	1.4980	45.62	65.41
2,3-Dibromohexane <sup>b,c</sup>	90 (16)	1.5812	1.5025	45.62	65.46
2,3-Dibromo-4-methylpentane	78 (22)	1.5996	1.5070	45.38	65.24
		(from high-boiling isomer)			
2,3-Dibromo-4-methylpentane	72–73 (18)	1.5983	1.5060	45.37	65.38
		(from low-boiling isomer)			
3,4-Dibromohexane <sup>d</sup>	80–81 (13)	1.6027	1.5045	45.14	65.38
1,3-Dibromo-2-methylpentane	87–88 (20)	1.5581	1.5015	46.11	64.38
1,2-Dibromo-2,3-dimethylbutane	80 (17)	1.6033	1.5105	45.58	64.75
1,2-Dibromo-2-ethylbutane <sup>e</sup>	87 (21)	1.6045	1.5112	45.60	65.12
2,3-Dibromo-2-methylpentane <sup>f</sup>	71–72 (18)	1.5849	1.5063	45.62	65.33

<sup>a</sup> Kirmann, *Bull. soc. chim.*, **39**, 988 (1926). <sup>b</sup> V. Risseghem, *Bull. soc. chim. Belg.*, **35**, 328 (1926). <sup>c</sup> Klarfeld, *Monatsh.*, **26**, 84 (1905). <sup>d</sup> Lespieau and Wiemann, *Bull. soc. chim.*, **48**, 627 (1929). <sup>e</sup> Kon, *J. Chem. Soc.*, **119**, 810 (1921). <sup>f</sup> Jawein, *Ann.*, **195**, 255 (1879).

### Summary

The nuclear synthesis of olefins through the  $\beta$ -bromo ethers has been used in a systematic survey of the hexenes. Ten of the thirteen structurally possible members of this family have been prepared, including those previously unknown. The method is shown to be applicable to the synthesis of monoalkyl, symmetrical and unsymmetrical dialkyl ethylenes. It is believed the method will ultimately prove applicable also to the trialkyl and tetraalkyl ethylenes.

The confusion which has existed in the physical constants of the olefins is beginning to disappear. A definite relation is shown to exist between the physical properties and molecular structure of the hexenes. Certain rules have been formulated relating the boiling points, densities and refractive indices of the hexenes to their structure.

Eight bromohexyl ethyl ethers, three hexenes and five dibromohexanes are herein described for the first time.

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## STUDIES OF POLYMERIZATION AND RING FORMATION. X. THE REVERSIBLE POLYMERIZATION OF SIX-MEMBERED CYCLIC ESTERS

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Reactions leading to the formation of high polymers have received considerable attention during the past few years both because of their inherent interest as representatives of a realm that has been relatively little explored, and because of their bearing on the formulation of naturally occurring macromolecular materials. In this connection the behavior of six-membered cyclic esters is of peculiar interest: they combine with themselves, in many cases spontaneously at the ordinary conditions, to form polymers of high molecular weight, and this transformation is reversible. Since these esters are generally free from unsaturation, their self-combination must have its origin in some peculiarity of the heterocyclic system. Six-membered heterocycles are quite common among naturally occurring materials and are closely associated with natural polymers (sugars and polysaccharides, diketopiperazines and polypeptides); it is therefore reasonable to assume that the behavior of the cyclic esters lies closer to the natural processes that result in the formation of macromolecular substances than does the polymerization of unsaturated compounds, such as styrene, which have been more extensively studied.

Several isolated examples of the reversible polymerization of six-mem-