[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

Syntheses in the Olefin Series. IV.[1] The Heptenes[2]

BY FRANK J. SODAY[3] AND CECIL E. BOORD

The third paper of this series,[1d] described the use of the β-bromo ether synthesis of olefins in a systematic survey of the hexenes. Eleven of the thirteen possible hexenes had been prepared, two having been obtained in apparent *cis–trans* modifications. The same synthesis has now been used in a survey of the heptenes. Seventeen of the twenty-seven possible heptenes have been prepared, ten of this number being herein described for the first time. Two of the seventeen have also been found to exist in two modifications.

The heptenes prepared include: 1-heptene, 5-methyl-1-hexene, 4-methyl-1-hexene and 3-methyl-1-hexene, all monoalkyl derivatives of ethylene. The list also includes the five symmetrical dialkyl derivatives of ethylene; 2-heptene, 5-methyl-2-hexene, 4-methyl-2-hexene, 3-heptene and 2-methyl-3-hexene. These olefins of types I and II were prepared by the general synthesis previously described. The method involves a four step process as indicated below

$$\text{R—CH}_2\text{—CHO} \longrightarrow \text{R—CH}_2\text{—CHCl—OC}_2\text{H}_5 \longrightarrow \text{R—CHBr—CHBr—OC}_2\text{H}_5 \longrightarrow$$
$$\text{R—CHBr—CHR}'\text{—OC}_2\text{H}_5 \longrightarrow \text{R—CH=CH—R}'$$

The unsymmetrical dialkyl derivatives of ethylene: 2-methyl-1-hexene, 2,3-dimethyl-1-pentene, 2,4-dimethyl-1-pentene, 2-ethyl-1-pentene and 2-ethyl-3-methyl-1-butene, all heptenes of type III, were prepared by an extended synthesis through the unsaturated ethers.[1d] The extension may be indicated by the scheme

$$\text{CH}_2\text{Br—CHR—OC}_2\text{H}_5 \longrightarrow \text{CH}_2\text{=CR—OC}_2\text{H}_5 \longrightarrow \text{CH}_2\text{Br—CBr(R)—OC}_2\text{H}_5 \longrightarrow$$
$$\text{CH}_2\text{Br—C(R)R}'\text{—OC}_2\text{H}_5 \longrightarrow \text{CH}_2\text{=C(R)R}'$$

The bromo ether synthesis has again been extended to include the trialkyl derivatives of ethylene, type IV. This is made possible by beginning the synthesis with a *n*-aldehyde higher than acetaldehyde and continuing the reaction through the extended synthesis involving the α,β-unsaturated ethers. The steps are as follows

(a) $\text{CH}_3\text{—CH}_2\text{—CHO} + \text{C}_2\text{H}_5\text{OH} + \text{HCl} \longrightarrow \text{CH}_3\text{—CH}_2\text{—CHCl—OC}_2\text{H}_5 + \text{H}_2\text{O}$

(b) $\text{CH}_3\text{—CH}_2\text{—CHCl—OC}_2\text{H}_5 + \text{Br}_2 \longrightarrow \text{CH}_3\text{—CHBr—CHBr—OC}_2\text{H}_5 + \text{HCl}$

(c) $\text{CH}_3\text{—CHBr—CHBr—OC}_2\text{H}_5 + \text{R—Mg—Br} \longrightarrow \text{CH}_3\text{—CHBr—CHR—OC}_2\text{H}_5 + \text{MgBr}_2$

(d) $\text{CH}_3\text{—CHBr—CHR—OC}_2\text{H}_5 + \text{KOH} \longrightarrow \left\{\begin{array}{l}\text{CH}_2\text{=CH—CHR—OC}_2\text{H}_5 \\ \qquad\qquad\qquad + \text{KBr} + \text{H}_2\text{O} \\ \text{CH}_3\text{—CH=CR—OC}_2\text{H}_5\end{array}\right.$

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(1) For the earlier papers in this series see: (a) Swallen and Boord, THIS JOURNAL, **52**, 651 (1930); (b) Dykstra, Lewis and Boord, *ibid.*, **52**, 3396 (1930); (c) Shoemaker and Boord, *ibid.*, **53**, 1505 (1931); (d) Schmitt and Boord, *ibid.*, **54**, 751 (1932).

(2) Presented in part before the Organic Division of the American Chemical Society at the Indianapolis Meeting, April, 1931.

(3) This paper is abstracted from the dissertation presented by Frank J. Soday in partial fulfilment of the requirements for the degree of Doctor of Philosophy to the Faculty of the Graduate School of The Ohio State University, June, 1932.

(e) $CH_3{-}CH{=}CR{-}OC_2H_5 + Br_2 \longrightarrow CH_3{-}CHBr{-}CBr(R){-}OC_2H_5$

(f) $CH_3{-}CHBr{-}CBr(R){-}OC_2H_5 + R'{-}Mg{-}Br \longrightarrow CH_3{-}CHBr{-}C(R)R'{-}OC_2H_5 + MgBr_2$

(g) $CH_3{-}CHBr{-}C(R)R'{-}OC_2H_5 + Zn(Alc) \longrightarrow CH_3{-}CH{=}C(R)R' + C_2H_5O{-}ZnBr$

The latter application of the bromo ether synthesis was first made by Flory and one of us in the preparation of 3-methyl-2-pentene. It is now being made the subject of a special investigation the details of which will be presented in a later paper. For our present purposes it suffices to say that the lower boiling, β,γ-unsaturated ether obtained in step (d) is readily separated from the higher boiling α,β-derivative by fractional distillation. The low boiling isomer forms the lesser portion of the total product. The α,β-unsaturated ether, which forms the major portion, may also be fractionated into two modifications. In the present work this latter separation was not made, but the total α,β-derivative was brominated and carried through steps (e, f and g) as previously described. The trialkyl derivatives of ethylene, 3-methyl-2-hexene, 3,4-dimethyl-2-pentene and 2-ethyl-2-pentene, were prepared by this extended procedure.

The Physical Constants of the Heptenes.—The physical constants such as boiling point, density, refractive index and molecular refractivity of the heptenes prepared from the bromo ethoxyheptanes are set forth in Table I in comparison with values taken from the literature. Space does not permit the tabulation of all the recorded data, but those values have been selected where special emphasis has been laid upon purity of product.

Identification and Analysis.—For the purpose of identification and analysis each of the eighteen heptenes was converted into the dibromide, which was purified and analyzed for bromine, see Table IV.

In a few cases where some doubt was felt as to their purity the original heptenes were regenerated from the dibromides. In every case the physical constants of the regenerated heptene checked closely with those of the product obtained directly from the bromo ether, as is shown in Table V.

In other cases where it seemed possible a rearrangement of the carbon skeleton might have taken place, the heptenes were hydrogenated to the corresponding heptanes and their physical constants compared with those recorded by Edgar, Calingaert and Marker.[4] The agreement was remarkably good in every case (see Table VI).

Experimental Part

α-Chloroalkyl Ethyl Ethers, $R{-}CHCl{-}OC_2H_5$.—The α-chloro ethers used in this investigation were all previously known[5] and were prepared by the method described by Shoemaker and one of us.[1c]

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[4] Edgar, Calingaert and Marker, THIS JOURNAL, **51**, 1485 (1929).

[5] Our attention has been called by Dr. H. R. Henze to the fact that α-chloroisobutyl ethyl ether described in the third paper of this series, Ref. 1d, was previously described by Gauthier, *Ann. chim. phys.*, [8] **16**, 313 (1909). We wish, at this time, to acknowledge the oversight.

Table I

Physical Constants[a] of the Heptenes

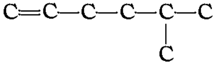
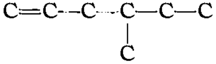
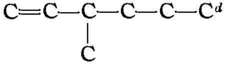
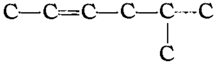
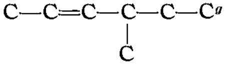
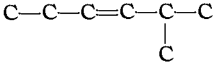
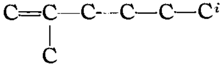
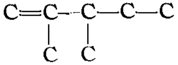
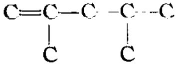
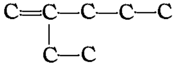
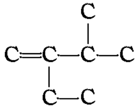
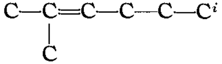
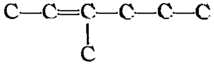
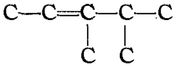
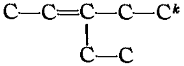
Structure	Type	B. p., °C. (760 mm.)	d_4^{20}	n_D^{20}	M. R. (calcd.) (34.06)	Investigator
$\mathrm{C{=}C{-}C{-}C{-}C{-}C{-}C}$	I	94.9	0.6993	1.3999	34.00	Present paper
		93.5–94.5	.6977	1.3976	33.82	Wilkinson[b]
 $\mathrm{C{=}C{-}C{-}C{-}\underset{\substack{\vert\\C}}{C}{-}C}$	I	84.7	.6936	1.3954	33.94	Present paper
		85–86	$.7160^{15}_{15}$			Brooks and Humphrey[c]
 $\mathrm{C{=}C{-}C{-}\underset{\substack{\vert\\C}}{C}{-}C{-}C}$	I	87.2–87.5	.6969	1.3985	34.01	Present paper
 $\mathrm{C{=}C{-}\underset{\substack{\vert\\C}}{C}{-}C{-}C{-}C}^{d}$	I (a)	83.8–84.0	.6953	1.3970	33.98	Present paper
	(b)	84.0–84.1	.6945	1.3970	34.02	Present paper
$\mathrm{C{-}C{=}C{-}C{-}C{-}C{-}C}$	II	98.1–98.4	.7034	1.4041	34.04	Present paper
		98.5				Schorlemmer and Thorpe[e]
 $\mathrm{C{-}C{=}C{-}C{-}\underset{\substack{\vert\\C}}{C}{-}C}$	II (H. B.)	91.1–91.6	.6990	1.3990	33.95	Present paper
	(L. B.)	85.6–86.1	.7020	1.3995	33.84	Present paper
		91	$.7060^{16}$			Grimshaw[f]
 $\mathrm{C{-}C{=}C{-}\underset{\substack{\vert\\C}}{C}{-}C{-}C}^{g}$	II (H. B.)	87.1–87.6	.7007	1.3980	33.79	Present paper
	(L. B.)	85.1–85.6	.6981	1.4000	34.07	Present paper
$\mathrm{C{-}C{-}C{=}C{-}C{-}C{-}C}$	II	95.8–96.1	.7043	1.4090	34.44	Present paper
		95.8_{763}	.7016	1.40419	34.169	Mathus and Gibon[h]
 $\mathrm{C{-}C{-}C{=}C{-}\underset{\substack{\vert\\C}}{C}{-}C}$	II	86.4–86.9	.6942	1.3991	34.19	Present paper
 $\mathrm{C{=}\underset{\substack{\vert\\C}}{C}{-}C{-}C{-}C{-}C}^{i}$	III	91.1–91.5	.7000	1.4040	34.28	Present paper
		$92.0–92.5_{753}$	.7033	1.4044^{18}	34.08	Zelenski and Przhevalskí
 $\mathrm{C{=}\underset{\substack{\vert\\C}}{C}{-}\underset{\substack{\vert\\C}}{C}{-}C{-}C}$	III	84.1–84.3	.7054	1.4022	33.88	Present paper
 $\mathrm{C{=}\underset{\substack{\vert\\C}}{C}{-}C{-}\underset{\substack{\vert\\C}}{C}{-}C}$	III	80.9–81.3	.6937	1.3970	34.06	Present paper

TABLE I (*Concluded*)

Structur	Type	B. p., °C. (760 mm.)	d_4^{20}	n_D^{20}	M. R. (calcd.) (34.06)	Investigator
 $C{=}\underset{C-C}{C}-C-C-C$	III	93.9–94.3	0.7079	1.4050	33.88	Present paper
 $C{=}\underset{C-C}{C}-\overset{C}{C}-C$	III	88.7–89.1	.7186	1.4120	33.97	Present paper
 $C-\underset{C}{C}{=}C-C-C-C^{i}$	IV	94.4–94.6 $93–94_{749}$ 92–95	.7089 .7080 $.7089^{20}$	1.4075 $1.4088^{20.5}$	34.11 34.12	Present paper Zelenski and Przhevalski Hurd and Bennett
 $C-C{=}\underset{C}{C}-C-C-C$	IV	93.1–93.3 85–90	.7120 $.7301_4^{25}$	1.4080 1.41319_D^{25}	33.99 33.49	Present paper Bjelous[j]
 $C-C{=}\underset{C}{C}-\underset{C}{C}-C$	IV	86.2–86.4	.7126	1.4052	33.76	Present paper
 $C-C{=}\underset{C-C}{C}-C-C^{k}$	IV	94.8–94.9 $95.0–95.5_{745}$ 96_{764}	.7172 $.7190_{25}^{25}$ $.7191_4^{24.45}$	1.4120 1.4128_D^{25} 1.4139	34.04 34.16 33.88	Present paper Lucas Böeseken and Wilschut

[a] The physical constants measured by the authors were in all cases measured under the conditions indicated at the top of the column. The constants taken from the literature, when measured under other conditions, are specifically so indicated in the table.

[b] Wilkinson, *J. Chem. Soc.*, 3058 (1931). See also Kirrmann, *Bull. soc. chim.*, [4] **39**, 990 (1926); and Bourguel, *ibid.*, [4] 41, 1475 (1927).

[c] Brooks and Humphrey, THIS JOURNAL, **40**, 834 (1918).

[d] The preparation of 3-methyl-1-hexene through the bromo ether formed by the action of 2-pentylmagnesium bromide upon α,β-dibromoethyl ethyl ether gives no difficulty. An attempt to prepare 3-ethyl-1-pentene, b. p. 85; d_4^{20} 0.6948; n_D^{20} 1.3966; M. R. 33.94 [Prévost, *Compt. rend.*, **187**, 946 (1928)], through the bromo ether obtained by the action of 3-pentylmagnesium bromide upon α,β-dibromoethyl ethyl ether yielded a heptene having almost identically the same physical constants as 3-methyl-1-hexene. Since it is well known that 3-bromopentane readily rearranges to 2-bromopentane [Lucas and Moyse, THIS JOURNAL, **47**, 1459 (1925); and Sherrill, Otto and Pickett, *ibid.*, **51**, 3023 (1929)] it seems obvious such a rearrangement had taken place either in the preparation of the alkyl bromide or during the formation of the alkylmagnesium halide. The physical constants for both products are recorded in Table I. Product (a) was obtained through 2-bromopentane and product (b) through 3-bromopentane. That they are identical is proven by the fact that hydrogenation over catalytic nickel gave the same heptane, 2-methylpentane, as shown in Table VI.

[e] Schorlemmer and Thorpe, *Ann.*, **217**, 150 (1883).

[f] 5-Methyl-2-hexene, as prepared through the corresponding bromo ether, is obtained in two forms. The low boiling portion (L. B.) equaled about 15% and the higher boiling portion (H. B.) about 85% of the total product. This heptene is cited in the third edition of Beilstein's Handbuch but omitted from the fourth edition. The earlier references are to the work of Schorlemmer [*Ann.*, **166**, 177 (1873)] and of Grimshaw [*ibid.*, 166, 167 (1873)], neither of whom specifically indicated the structure of their product. The higher boiling portion recorded in Table I may be identical with the heptene previously described.

[g] 4-Methyl-2-hexene was also obtained in two forms. In this case the low boiling portion (L. B.) equals about 20% of the total product. The higher boiling portion (H. B.) bears a marked resemblance to 4-methyl-1-hexene but the dibromides of these two heptenes are distinctly different, showing the identity to be only apparent.

[h] Mathus and Gibon, *Bull. soc. chim. Belg.*, **34**, 303 (1925); see also Bourguel, *Ann. chim.*, 3, 372 (1925), and Prévost, *ibid.* This heptene as obtained by the bromo ether method has a higher density and a higher refractive index than is found for the same olefin when prepared by other methods. The discrepancy is being further investigated.

[i] Zelenski and Przhevalski, *J. Russ. Phys.-Chem. Soc.*, **39**, 1169 (1907); **40**, 1105 (1908); Hurd and Bennett, THIS JOURNAL, **51**, 3675 (1929). 2-Methyl-1-hexene and 2-methyl-2-hexene form a pair of heptenes which have been much confused. Many of the methods commonly used for the preparation of olefins yield a mixture when applied to these two hydrocarbons. Zelenski and his co-workers believed 3-heptene also to be a component of this mixture. Space does not permit a discussion of the merits of the several points of view which have been advanced with regard to the rearrangements involved. When the bromo ether synthesis for the olefins of type three is applied to 2-methyl-1-hexene the product is free from isomers.

The bromo ether synthesis has not yet been applied to 2-methyl-2-hexene, an olefin of type IV. The physical constants recorded in Table I were measured on a product prepared from dimethyl-*n*-butylcarbinol by dehydration over anhydrous oxalic acid. This product has a remarkably constant boiling point and upon hydrogenation yielded 2-methylhexane as is shown in Table VI.

[j] Bjelous, *Ber.*, 45, 629 (1912).

[k] Lucas, THIS JOURNAL, **51**, 248 (1929); Böeseken and Wilschut, *Rec. trav. chim.*, **51**, 171 (1932).

α,β-Dibromoalkyl Ethyl Ethers, R—CHBr—CHBr—OC_2H_5.—The dibromo ethers were prepared by two methods, both of which have been described in previous communications. Those used in the synthesis of the olefins of types I and II were obtained by the direct bromination of the corresponding α-chloro ethers.[1a] Those used in the synthesis of the olefins of types III and IV were secured by the addition of bromine to the appropriate α,β-unsaturated ether.[1d]

Unsaturated Ethers, R—CH=C(OEt)—R'.—The α,β-unsaturated ethers were prepared by the method of Lauer and Spielman.[6] The detailed procedure described in Ref. 1d was followed except that the Hempel tube was replaced by a 30.5-cm. Vigreux column, thereby effecting a more complete separation of the product from the unchanged β-bromo ether. When the β-bromo ethers derived from propionaldehyde are used one obtains both the α,β- and the β,γ-unsaturated ethers. The latter compounds having exposed double bonds boil markedly lower and are easily separated from the α,β-derivatives. The relative yields of 3-ethoxy-1-butene and 3-ethoxy-2-butene were 31 and 48% and of 3-ethoxy-1-pentene and 3-ethoxy-2-pentene were 22 and 72%, respectively.

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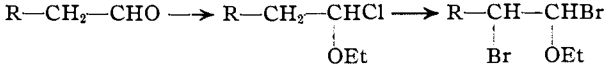
(6) Lauer and Spielman, THIS JOURNAL, **53**, 1533 (1931).

The composite yields of α-chloro ethers, dibromo ethers and unsaturated ethers, as based on the aldehydes used, are shown in Table IIA. The yields given are the average for the number of runs indicated parenthetically.

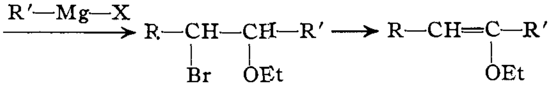
TABLE IIA

YIELD OF α-CHLORO, α,β-DIBROMO, β-BROMO AND α,β-UNSATURATED ETHERS



$$R{-}CH_2{-}CHO \longrightarrow R{-}CH_2{-}\underset{OEt}{CHCl} \longrightarrow R{-}\underset{Br}{CH}{-}\underset{OEt}{CHBr}$$

(R)	H	CH_3	C_2H_5	$(CH_3)_2$
Yield, %	79.3 (30)	71 (12)	86 (4)	81 (2)
Yield, %	95 (27)	93 (14)	92 (4)	89 (2)



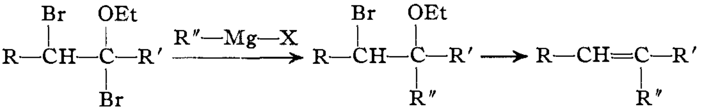
$$\xrightarrow{R'{-}Mg{-}X} R{-}\underset{Br}{CH}{-}\underset{OEt}{CH}{-}R' \longrightarrow R{-}CH{=}\underset{OEt}{C}{-}R'$$

(R')	CH_3	C_2H_5	CH_3	C_2H_5
Yield, %	52 (5)	48.2 (5)	73.6 (5)	40 (3)
Yield, %	64 (3)	67 (3)	48 (1)	72 (1)

β-Bromoethoxyheptanes, R—CH(Br)—C(OEt)R'R".—The β-bromo ethers were prepared by the procedure described in the earlier papers of this series. In general it may be said that the primary alkylmagnesium halides give better yields than the secondary derivatives and that the condensation of a tertiary alkylmagnesium halide has not been in any case successful. The β-bromo ether synthesis is restricted at one other point: aldehydes, such as isobutyraldehyde, which have a branching chain

TABLE IIB

YIELD OF BROMO ETHOXYHEPTANES AND CORRESPONDING HEPTENES



$$R{-}\overset{Br}{CH}{-}\underset{Br}{\overset{OEt}{C}}{-}R' \xrightarrow{R''{-}Mg{-}X} R{-}\overset{Br}{CH}{-}\underset{R''}{\overset{OEt}{C}}{-}R' \longrightarrow R{-}CH{=}\underset{R''}{C}{-}R'$$

(R)	(R')	(R")	Yield, %	Yield, %	Over-all yield on aldehyde, %
H	H	n-C_5H_{11}–	61–66	80–88	36.8–43.8
H	H	iso-C_5H_{11}–	55	70	29
H	H	C_2H_5–$CH(CH_3)$–CH_2–	60	72	32.5
H	H	n-C_3H_7–$CH(CH_3)$–	22–36	75–64	12.4–20.3
CH_3	H	n-C_4H_9–	69	77	35.0
CH_3	H	iso-C_4H_9–	49	91	29.4
CH_3	H	sec-C_4H_9–	31	92	18.4
C_2H_5	H	n-C_3H_7–	30–32	87	17.2–18.4
C_2H_5	H	iso-C_3H_7–	20–35	78	10.3–18.0
H	CH_3	n-C_4H_9–	35	66	5.6
H	CH_3	iso-C_4H_9–	42	66	7.0
H	CH_3	sec-C_4H_9–	21–25	66–54	2.8– 4.1
H	C_2H_5	n-C_3H_7–	30	62	4.5
H	C_2H_5	iso-C_3H_7–	42	84	8.6
CH_3	CH_3	n-C_3H_7–	26	75	4.5
CH_3	CH_3	iso-C_3H_7–	22	60	3.1
CH_3	C_2H_5	C_2H_5–	40	69	5.3

alpha to the aldehyde group, give only poor yields of β-bromo ethers. In such a case the product carried over by steam distillation contains an appreciable amount of low boiling material. This low boiling portion consists in part of the bromo aldehyde formed by the hydrolysis of the residual dibromo ether, in part of the unsaturated bromo ether formed by the loss of hydrogen bromide (alpha bromine) from the dibromo derivative and in certain cases to the formation of a β-bromo ether of lower molecular weight due to the reducing action of the Grignard reagent. The yields of the individual bromo ethoxyheptanes are shown in Table IIB and their physical constants and analyses in Table III.

The Heptenes.—The β-bromoethoxyheptanes were converted into the corresponding heptenes by the action of zinc dust on the isopropyl alcohol solution. Approximately 100 g. of zinc dust and an equal weight of isopropyl alcohol were used for each quarter mole of the bromo ether. The digestion was continued under a reflux condenser at the boiling point of the solvent for lengths of time varying from eight to ninety-six hours. A re-working of some of the residual reaction mixtures showed an improvement in the yield up to forty-eight hours. The propyl alcohol–heptene mixture was distilled from the residual zinc and diluted with from eight to ten volumes of cold water. The lighter hydrocarbon layer was separated, washed repeatedly with an equal volume of cold water and dried over granular calcium chloride. The purified heptene was then repeatedly digested and distilled over metallic sodium until there was no further indication of reaction. The final product was fractionated through a 30.5 cm. Vigreux column, the major portion usually being collected with a boiling range of less than 0.5°. During the latter part of the investigation a 46-cm. column having a dephlegmating head was used. The ratio of return down the column to the take-off rate was adjusted to approximately 10 to 1. Under these conditions the boiling range was usually less than 0.3°.

TABLE III

BROMOETHOXYHEXANES

Name Bromo, Ethoxy	B. p., °C. (mm.)	d^{20}_{D}	n^{20}_{D}	M. R. (calcd.) (53.2)	Anal., Br, % (calcd.) (35.87)	
1-()-2-()-heptane	89.9–90.8 (8)	1.1210	1.4530	53.8	35.99	36.19
1-()-2-()-5-methylhexane[1a]	164.6 (250)	1.1189	1.4476	53.3	35.97	36.02
1-()-2-()-4-methylhexane	88.5–89.5 (10)	1.1155	1.4500	53.7	35.97	36.02
1-()-2-()-3-methylhexane	75–76 (1.5) 102–104 (21)	1.1179	1.4444	53.0	35.97	36.00
2-()-3-()-heptane	90–91 (13) 95.5–96.5 (15)	1.0986	1.4420	53.7	35.84	36.02
2-()-3-()-5-methylhexane	91.0–92.0 (19)	1.1142	1.4489	53.5	35.79	35.81
2-()-3-()-4-methylhexane	89–90 (15)	1.0943	1.4435	54.1	35.40	35.51
3-()-4-()-heptane	88.0–89.0 (13.5) 90.0–91.0 (15)	1.1063	1.4425	53.3	35.80	35.88
3-()-4-()-5-methylhexane	88.0–90.0 (15)	1.1225	1.4528	53.7	35.70	35.58
1-()-2-()-2-methylhexane	103–104 (22)	1.1270	1.4540	53.6	35.96	35.50
1-()-2-()-2,3-dimethylpentane	75.5–76.5 (4)	1.1545	1.4600	52.9	25.72	35.93
1-()-2-()-2,4-dimethylpentane	72–73 (3)	1.1544	1.4608	53.0	36.15	36.11
1-()-2-()-2-ethylpentane	73.0–75.0 (6)	1.1550	1.4590	52.8	35.07	34.99
1-()-2-()-2-ethyl-3-methylbutane	66–68	1.1488	1.4588	53.1	35.71	35.70
2-()-3-()-3-methylhexane	69.0–70.0 (3)	1.1601	1.4628	53.0	35.86	35.89
2-()-3-()-3,4-dimethylpentane	71–72 (3)	1.1929	1.4700	52.2	36.28	36.41
2-()-3-()-3-ethylpentane	69–70 (3)	1.1534	1.4620	53.2	35.82	35.80

TABLE IV

DIBROMOHEPTANES

Name	B. p., °C. (mm.)	d_4^{20}	n_D^{20}	M. R. (calcd.) (50.05)	Anal., Br, % (calcd.) (61.95)	
1,2-Dibromoheptane[16]	106.2 (13)	1.5208	1.4990	49.80	61.95	62.22
1,2-Dibromo-5-methylhexane[1a]	142.6–143.6 (101)	1.5072	1.4970	50.08	61.90	61.94
1,2-Dibromo-4-methylhexane	94.7–95.7 (11)	1.5027	1.4980	50.31	61.47	61.50
1,2-Dibromo-3-methylhexane	84.0–84.2 (6)	1.5248	1.5028	49.99	61.81	62.02
2,3-Dibromoheptane	96.2 (12)	1.5129	1.5000	50.15	61.98	61.91
2,3-Dibromo-5-methylhexane (H. B.)	89–90 (11)	1.5152	1.4990	49.98	61.71	61.47
(L. B.)	87–88 (10)	1.5027	1.4960	50.14	61.62	61.60
2,3-Dibromo-4-methylhexane	91–92 (11)	1.5382	1.5045	49.70	61.62	61.59
3,4-Dibromoheptane[17]	105.5–106.5 (23)	1.5153	1.5010	50.15	61.96	61.82
3,4-Dibromo-2-methylhexane	96.0 (19)	1.5310	1.5060	50.05	61.82	61.82
1,2-Dibromo-2-methylhexane	100.5–101.5 (23) 71.0–71.1 (3)	1.5066	1.5000	50.35	61.99	61.93
1,2-Dibromo-2,3-dimethylpentane	72.5–73.0 (3)	1.5245	1.5028	50.00	61.98	61.97
1,2-Dibromo-2,4-dimethylpentane	65.5–66.0 (4)	1.5136	1.5005	50.16	61.97	61.93
1,2-Dibromo-2-ethylpentane	77–78 (4)	1.4929	1.4990	50.73	61.60	61.67
1,2-Dibromo-2-ethyl-3-methylbutane	72.5–73.5 (3)	1.5261	1.5062	50.23	61.17	61.67
2,3-Dibromo-2-methylhexane	73.0–73.1 (8)	1.5116	1.4990	50.09	61.94	61.98
2,3-Dibromo-3-methylhexane[18]	65.0–65.1 (2)	1.5240	1.5040	50.12	62.08	62.35
2,3-Dibromo-3,4-dimethylpentane	65.5–66.0 (3)	1.5400	1.5104	50.13	61.93	61.85
2,3-Dibromo-3-ethylpentane	76.0–76.4 (3)	1.5426	1.5090	49.94	61.59	61.67

[16] (a) Venable, THIS JOURNAL, **4**, 22 (1882); (b) see also Refs. 4, f, h, j; 10 a.

[17] Limpricht, *Ann.*, **103**, 86 (1857).

[18] (a) Ipatiew, *J. Russ. Phys.-Chem. Soc.*, **27**, 373 (1895); *J. prakt. Chem.*, [2] **53**, 285 (1896). (b) Mereshkavski, *J. Russ. Phys.-Chem. Soc.*, **45**, 1970 (1913).

The Dibromoheptanes, $C_7H_{14}Br_2$.—The heptene was placed in solution in anhydrous ether or chloroform and immersed in a mixture of ice and salt, the theoretical amount of bromine being slowly added with vigorous stirring. The absorption of bromine was instantaneous and quantitative. The solvent was distilled off on the water-bath, the residual dibromoheptane dried over calcium chloride and fractionated under diminished pressure. The physical constants and analyses of the dibromoheptanes are shown in Table IV.

Reconversion of Dibromoheptanes into Heptenes.—In the case of 2,3-dimethyl-1-pentene and 3-ethyl-2-pentene the purity of the product obtained directly from the bromo ether synthesis was not wholly satisfactory. In order to secure a product of higher purity the corresponding dibromides after purification were reconverted into the original heptenes. The dibromoheptanes were dissolved in from two to three times their weight of absolute alcohol and digested at the boiling point under a reflux condenser with approximately twice their weight of zinc dust for several hours. The conversion of the dibromides takes place much more rapidly than when the bromo ethers are used so that a much shorter time is required. The experimental data for the preparation and the boiling points of these regenerated heptenes are shown in Table V.

TABLE V

HEPTENES REGENERATED FROM DIBROMOHEPTANES

Heptene	Method	B. p., °C. (mm.)	B. p. (calcd. 760)
2,3-Dimethyl-1-pentene	β-Bromo ether	83.4–83.6 (744)	84.1–84.3
	β-Bromo ether	83.6–84.0 (750)	84.0–84.4
	Dibromide	83.2–83.5 (740)	84.1–84.4
2-Ethyl-3-methyl-1-butene	β-Bromo ether	87.9–88.3 (748)	88.4–88.8
	Dibromide	88.2–88.5 (747)	88.7–89.1
2,4-Dimethyl-1-pentene	β-Bromo ether	80.4–80.8 (748)	80.9–81.3
	Dibromide		80.9–81.3
3-Ethyl-2-pentene	β-Bromo ether	94.5–94.7 (743.5)	95.3–95.5
	Dibromide	93.9–94.0 (740.7)	94.8–94.9

Conversion of Heptenes to Heptanes.—Four of the heptenes were hydrogenated by the method of Edgar, Calingaert and Marker to the corresponding heptanes. The conversion was high in every case and the physical constants of the heptanes obtained agree closely with those recorded by the above investigators, as is shown by the data tabulated in Table VI.

TABLE VI

HEPTANES FORMED BY THE HYDROGENATION

Heptane	B. p., °C. (760 mm.)	d_4^{20}	n_D^{20}	M. R.	Investigator
n-Heptane from (2-heptene)	98.4	0.6830	1.3870	34.47	Present paper
	98.4	.6836	1.38777	34.54	E. C. and M.[4]
2-Methylhexane from (2-methyl-2-hexene)	89.7–89.8	.6786	1.3850	34.57	Present paper
	90.0	.6789	1.38509	34.57	E. C. and M.
2,3-Dimethylpentane from (2,3-dimethyl-1-pentene)	91.6–91.7	.6888	1.3885	34.29	Present paper
	91.8	.6870	1.38873	34.31	E. C. and M.
3-Methylhexane from (3-methyl-1-hexene)	89.3–89.4	.6957	1.3933	34.38	Present paper
	89.7	.6952	1.39201	34.45	E. C. and M.

The physical characteristics of five of the remaining nine heptenes have already been recorded in the literature. Experimental data relating to three others are more or less completely in hand and will be offered for publication at an early date. The remaining member of this group, 3,4-dimethyl-1-pentene, is proving more difficult but may yet be obtained.

Space has not permitted an adequate discussion of the remarkable correlation between the physical properties and the structure of the above heptenes such as has been included in the earlier papers of this series. Such a discussion will form a part of a more general paper taking up this question as it relates to the olefins.

Summary

The bromo ether synthesis has been applied in a systematic survey of the heptenes. Eighteen of the twenty-seven heptenes are herein described, seventeen having been obtained by the above synthesis. Ten of these heptenes are new.

The seventeen corresponding bromoethoxyheptanes and eighteen dibromoheptanes, prepared incidentally to the synthesis and identification of the above heptenes, are also described. Sixteen of the ethoxy derivatives and fourteen of the dibromides are new.

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Furan Mercurials

BY HENRY GILMAN AND GEORGE F. WRIGHT

Introduction

Apparently the only published study on pure furan mercurials is that by Ciusa and Grillo,[1] who prepared tetraacetoxy- and tetrachloromercurifurans, from which they obtained tetraiodofuran. They also reported the isolation of acetoxymercurifuran and chloromercurifuran by the action of mercuric salts on furoic acid, but they were unable to repeat the preparation of these mono-mercurials.

We find that a wide variety of furan mercurials can be conveniently prepared either by direct nuclear substitution or by replacement of a carboxyl group. The mercurials are reagents of choice for two purposes. First, they admirably bridge the gap between the unusually reactive and unusually inert substituted furans[2] and so render more accessible, by subsequent replacement reactions, important furan types. Second, they constitute at this time the best derivatives for the characterization of many furans, and for the stabilization of sensitive furans.

(1) Ciusa and Grillio, *Gazz. chim. ital.*, **57**, 323 (1927). See, also, Shepard, Winslow and Johnson, THIS JOURNAL, **52**, 2083 (1930) for the preparation of a mixture of mercuration products from furoic acid; and the paper by Scheibler and co-workers, *J. prakt. chem.*, **136**, 232 (1933), which appeared just prior to receipt of proof, on the mercuration of furfural diacetate.

(2) Gilman and Young, *Rec. trav. chim.*, **51**, 761 (1932).