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

A NUCLEAR SYNTHESIS OF UNSATURATED HYDROCARBONS.
I. ALPHA-OLEFINS[1,2]

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In a recent paper by Lloyd C. Swallen[3] and one of us, a method was suggested for the synthesis of olefins. This method has been developed and perfected to the point where it now promises to be of real service in the study of unsaturated hydrocarbons. The necessity for revision and extension of our knowledge of these hydrocarbons has frequently been pointed out.[4] This necessity arises not only from the increasing industrial use of these compounds but also from the fact that much of the previous literature has been found to be in error.

The more recent investigations in so far as they relate to α-olefins give boiling points lower than those previously given. Brochet,[5] Schorlemmer,[6] and Norris and Joubert[7] give 39–40° as the boiling point of pentene-1. On the other hand, Kirrmann[8] and Bourguel[9] give 30.5–31° and 32.5°, respectively. Brochet[5] gives 67° and van Beresteyn[10] 67.7–68.1° as the boiling point of hexene-1, while Brooks and Humphrey[11] give 60.5–61.5° and Miss van Risseghem[12] gives 63.35° ± 0.05° for the same compound. These variations are merely indicative of a confusion which is somewhat general in the literature of unsaturated hydrocarbons.

The differences in results obtained by different investigators may be attributed to a number of sources. As Brooks[13] has said: "High temperatures and many chemical reagents, particularly acids, cause such α-olefins to rearrange or the double bond to shift its position. Only re-

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[1] Presented in part before the division of Organic Chemistry at the meeting of the American Chemical Society in Detroit, Michigan, September 8, 1927.

[2] This paper is abstracted from the Dissertation of Harry B. Dykstra and in part from the Dissertation of J. Franklin Lewis as presented in partial fulfilment of the requirements of the degree of Doctor of Philosophy, to the Faculty of the Graduate School of The Ohio State University, June, 1927, and March, 1930, respectively.

[3] Swallen and Boord, THIS JOURNAL, **52**, 651 (1930).

[4] Brooks, "Non-Benzenoid Hydrocarbons," The Chemical Catalog Company, New York, **1922**, p. 158.

[5] Brochet, *Bull. soc. chim.*, [3] **7**, 567 (1892).

[6] Schorlemmer, *Ann.*, **161**, 269 (1872).

[7] Norris and Joubert, THIS JOURNAL, **49**, 873 (1927).

[8] Kirrmann, *Bull. soc. chim.*, **39**, 988 (1926).

[9] Bourguel, *ibid.*, **41**, 1475 (1927).

[10] Van Beresteyn, *Bull. soc. chim. Belg.*, **25**, 293 (1911).

[11] Brooks and Humphrey, THIS JOURNAL, **40**, 833 (1918).

[12] Van Risseghem, *Bull. soc. chim. Belg.*, **35**, 328 (1926).

[13] Ref. 4, p. 178.

actions employing low temperatures and the absence of isomerizing agents can be expected to produce α-olefins in any degree of purity..."

The preparation of α-olefins by low-temperature methods involves difficulties of another type. The condensation of an alkylmagnesium halide with allyl bromide in so far as it has been applied to the preparation of pentene-1[3,8] and hexene-1[11,12] introduces the necessity of purifying these products from the alkyl halides and ethers used in the condensation. The purification processes are long and tedious and are not always wholly successful. The reduction of the corresponding acetylene to an olefin by hydrogen in the presence of a catalyst[10] involves the inherent possibility of the simultaneous formation of the corresponding saturated hydrocarbon.

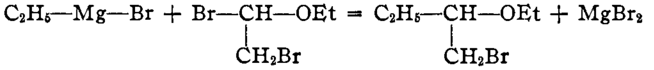
The synthesis described in this paper is not entirely free from such difficulties. The products prepared have the usual olefin characteristics in that they are not directly obtained in a high degree of purity. The method does, however, seem to yield products possessing the structure indicated by the synthesis.

No attempt has been made in the present work to apply the high degree of refinement used by Miss van Risseghem[12] in her excellent work on hexene-1 and hexene-2. Work of this character requires the production of several hundred grams of each product. The process described will ultimately lend itself to such studies. For the present our efforts have been confined to the perfection of the method and a description of those products which have not yet been adequately described.

The nuclear synthesis is a four step process. The first three steps lead to the preparation of a series of β-ethoxy-alkyl bromides (β-bromo ethers). Its application to the synthesis of pentene-1 is shown by the following scheme

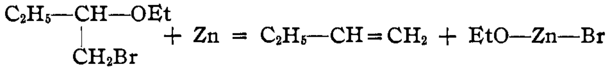
$$CH_3\text{—}CHO + EtOH + HCl = CH_3\text{—}CHCl\text{—}OEt + H_2O \qquad (1)$$

$$CH_3\text{—}CHCl\text{—}OEt + Br_2 = CH_2Br\text{—}CHBr\text{—}OEt + HCl \qquad (2)$$



$$C_2H_5\text{—}Mg\text{—}Br + Br\text{—}\underset{\substack{|\\ CH_2Br}}{CH}\text{—}OEt = C_2H_5\text{—}\underset{\substack{|\\ CH_2Br}}{CH}\text{—}OEt + MgBr_2 \qquad (3)$$

In the fourth step zinc is used for the simultaneous removal of the ethoxy group and bromine in a manner similar to that used by Gladstone and Tribe[14] for regenerating an olefin from its dibromide.



$$C_2H_5\text{—}\underset{\substack{|\\ CH_2Br}}{CH}\text{—}OEt + Zn = C_2H_5\text{—}CH{=}CH_2 + EtO\text{—}Zn\text{—}Br \qquad (4)$$

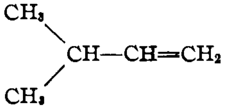
It has been found advisable to avoid fractionation of the halogenated ethers obtained in steps one and two because of loss in yield by decomposition. The β-bromo ethers obtained in step three are quite stable and may be completely purified. The formation of the olefin in step four is slow but the yields are satisfactory.

[14] Gladstone and Tribe, *Ber.*, **7**, 364 (1874); *J. Chem. Soc.*, **21**, 306 (1878).

Pentene-1, hexene-1, 4-methylpentene-1 (iso-α-hexene) and 5-methylhexene-1 (iso-α-heptene) have been prepared by the scheme outlined above. Of these the iso-α-hexene seems not to have been described previously. The other three were obtained with boiling points agreeing closely with those given for the same compounds when prepared by other low-temperature methods. Since Kirrmann on the one hand and Norris and Joubert on the other did not obtain the same results in the synthesis of pentene-1 by the action of ethylmagnesium bromide upon allyl bromide, this condensation has been carefully repeated a number of times. In every case, regardless of the method of purification used, a product boiling at 29–31° was obtained.[15]

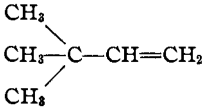
By combining steps three and four in the synthesis it has been possible to condense allyl bromide with α,β-dibromo-ethyl ether and to produce the heretofore unknown 1,4-pentadiene. This compound was purified by conversion into its crystalline tetrabromide, the diene being regenerated by the action of zinc on an alcoholic solution.

Some of the more recently determined values for the boiling points of the α-olefins, including those contained in the present paper, are shown in Table I for comparison with those of the corresponding β-olefins and saturated hydrocarbons. It will be noted that the boiling point of 1,4-pentadiene is lower than that of pentene-1 and this is in turn lower than that of *n*-pentane. Also that of 1,5-hexadiene is lower than that of hexene-1 and this is lower than *n*-hexane. Further, it will be noted that the boiling point of iso-α-pentene is lower than for isopentane, iso-α-hexene lower than isohexane and iso-α-heptene lower than isoheptane. From these facts one may tentatively formulate the following rule: an α-olefin of the type $R{-}CH{=}CH_2$ *boils lower than the corresponding saturated hydrocarbon.* The usual branching chain rule with respect to boiling points may be restated for olefins as follows: *in any given family of olefins the one having the most highly branching chain substituted on the ethylene group* ($-CH{=}CH_2$) *has the lowest boiling point.* Combining the two rules one sees that isopropylethylene, I, should be the lowest boiling of the pentenes and tertiary butylethylene, II, the lowest boiling hexene. An examination of the literature shows this to be the case.



$(CH_3)_2CH{-}CH{=}CH_2$

I



$(CH_3)_3C{-}CH{=}CH_2$

II

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[15] Dr. Mary L. Sherrill, of Mount Holyoke College, in a private communication, states that she also has prepared pentene-1 by the above method using the Kirrmann procedure. The product obtained had the following physical constants: m. p. (754 mm.) 30.5–31.0°; *d* 0.6419; n_D^{20} 1.3711.

Further examination of Table I shows that the boiling point of pentene-1 is lower than that of pentene-2, hexene-1 lower than hexene-2 and iso-α-hexene lower than iso-β-hexene.

TABLE I

BOILING POINTS OF α-OLEFINS

Hydrocarbon	B. p., °C.	Investigator
$CH_3-CH_2-CH_2-CH_2-CH_3$	36.3	Thorpe and Jones[a]; Young[b]
$CH_3-CH=CH-CH_2-CH_3$	36.4	Sherrill, Otto and Pickett[c]
	36.39	Norris and Reuter[d]
$CH_2=CH-CH_2-CH_2-CH_3$	30.5–31	Kirrmann[e]
	32.5	Bourguel[f]
	29.5–31, 30.2	Present paper
$CH_2=CH-CH_2-CH=CH_2$	29–30	Present paper
$CH_3-CH_2-CH(CH_3)_2$	27.95	Young and Thomas[g]
$CH_2=CH-CH(CH_3)_2$	20.5–20.7	Michael and Zeidler[h]
$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$	68.95	Young[i]
$CH_3-CH=CH-CH_2-CH_2-CH_3$	68.0–68.2	van Risseghem[k]
$CH_2=CH-CH_2-CH_2-CH_2-CH_3$	63.35	van Risseghem
	61–64	Present paper
$CH_2=CH-CH_2-CH_2-CH=CH_2$	59.57	Cortese[l]
$CH_3-CH_2-CH_2-CH(CH_3)_2$	60.2	van Risseghem[m]
$CH_3-CH=CH-CH(CH_3)_2$	58.15–59.15	van Risseghem
$CH_2=CH-CH_2-CH(CH_3)_2$	53–59	Present paper
$CH_3-CH_2-C(CH_3)_3$	49.6–49.7	Markownikow[n]
$CH_2=CH-C(CH_3)_3$	41.2	Delacre[o]
$CH_3-CH_2-CH_2-CH_2-CH(CH_3)_2$	89.9–90.4	Francis and Young[p]
$CH_2=CH-CH_2-CH_2-CH(CH_3)_2$	84–85	Brooks and Humphrey[q]
	85–86	André[r]
	84–86	Present paper

[a] Thorpe and Jones, *J. Chem. Soc.*, **63**, 290 (1893); [b] Young, *ibid.*, **71**, 446 (1897); [c] Sherrill, Otto and Pickett, THIS JOURNAL, **51**, 3023 (1929); [d] Norris and Reuter, *ibid.*, **49**, 2632 (1927); [e] Kirrmann, *Bull. soc. chim.*, **39**, 988 (1926); [f] Bourguel, *ibid.*, **41**, 1475 (1927); [g] Young and Thomas, *J. Chem. Soc.*, **71**, 440 (1897); [h] Michael and Zeidler, *Ann.*, **385**, 250 (1911); [i] Young, *J. Chem. Soc.*, **73**, 906 (1898); [k] van Risseghem, *Bull. soc. chim. Belg.*, **35**, 328 (1926); [l] Cortese, THIS JOURNAL, **51**, 2268 (1929); [m] van Risseghem, *Bull. soc. chim. Belg.*, **30**, 8 (1921); [n] Markownikow, *Ber.*, **32**, 1446 (1899); [o] Delacre, *Bull. acad. roy. med. Belg.*, 7–41 (1906); [p] Francis and Young, *J. Chem. Soc.*, **73**, 906, 922 (1898); [q] Brooks and Humphrey, THIS JOURNAL, **40**, 834 (1918); [r] André, *Ann. chim. phys.*, [8] **29**, 554 (1913).

Experimental Part

The Preparation of β-Bromo Ethers

A. **Alkyl-α-chloro-ethyl Ether, $R-O-CHCl-CH_3$.**—The method described by Swallen and one of us[3] has been generalized and extended to include the preparation of *n*-propyl- and *n*-butyl-α-chloro-ethyl ethers. It was found advisable for the purpose of synthesis to avoid distillation, the yield being diminished as much as 20 to 25% by a single fractionation. The reaction mixture separates into two layers. The upper ethereal layer is removed and dried over calcium chloride. For the α-chloro-ethyl ethers mentioned above the yield varies from 80 to 90% of crude or 60 to 69% of the distilled product.

B. **Alkyl-α,β-dibromo-ethyl Ethers**, R—O—CHBr—CH_2Br.—The alkyl-α-chloro-ethyl ethers were brominated by the procedure previously described. The crude reaction products may be submitted directly to distillation under diminished pressure but it was found advisable in this case also to avoid distillation. The hydrogen chloride was removed under diminished pressure or by aspirating a slow current of air through the reaction mixture. The yields vary from 93 to 95% of crude or 88.5 to 91% of distilled product. The physical constants and analyses of ethyl-, *n*-propyl- and *n*-butyl-α,β-dibromo-ethyl ethers are shown in Table II. The last two ethers have not been described previously.

TABLE II

α,β-DIBROMO-ETHYL ALKYL ETHERS, R—O—CHBR—CH_2BR

α,β-Dibromo-ethyl (*Alkyl*) Ethers	Yield, %	B. p., °C.	d_{20}^{20}	Analyses, Br, % Found	Calcd.
Ethyl	90.5	86 (31 mm.)	1.7370	68.89	68.92
n-Propyl	92.9[a]	97 (27 mm.)	1.6554	64.92	64.99
n-Butyl	95.2[a]	115 (36 mm.)	1.5647	61.15	61.49

[a] These yields are for crude products as used in the synthetic experiments.

Wislicenus, who[16] obtained the ethyl derivative by brominating the vinyl ethyl ether, says "it is not possible to obtain the pure product by fractional distillation since it decomposes upon heating with the evolution of hydrogen bromide and the formation of a black non-volatile tar." The analyses given in Table II are those obtained for the products after a single distillation. Repeated distillations tend to produce a lowering of the boiling point by decomposition.

C. **Alkyl-β-Bromo-ethyl Ethers, Condensation of α,β-Dibromo-ethyl Ether with an Alkylmagnesium Halide.**—In the earlier experiments the coupling was effected by adding the ether solution of the Grignard reagent to an anhydrous ether solution of the dibromo ether, in order to avoid the presence of residual magnesium. It was soon found that the products prepared in this way were difficult to purify. Since an excess of the alkylmagnesium halide increased both the yield and purity of the product, the later experiments were carried out using the same order of mixing the reagents that was used by Houben and Führer.[17]

The Grignard reagents were made in the usual manner. The flask was surrounded by ice water and the dibromo ether, dissolved in an equal volume of anhydrous ether, added through the dropping funnel at such a rate that the mixture remained cold. Mechanical stirring was used throughout and for fifteen minutes after the addition was completed. The reaction mixture was decomposed by pouring on ice and acidifying with dilute hydrochloric acid. The ether layer was separated, dried over calcium chloride, and the ether removed by distillation. The product was then transferred to a smaller flask, about 5% of its weight of solid sodium hydroxide added, and fractionated. β-Ethoxy-*n*-propyl bromide and β-ethoxy-*n*-butyl bromide may be distilled at atmospheric pressure but the higher members are best distilled under diminished pressure. The yields, physical constants and analyses of fourteen β-bromo ethers prepared by this procedure are given in Table III. The yields recorded in the table are those obtained after a single distillation and are calculated on the basis of the dibromo ether used.

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[16] Wislicenus, *Ann.*, **192,** 111 (1878).

[17] Houben and Führer, *Ber.*, **40,** 4993 (1907).

TABLE III

β-ALKOXY-ALKYL BROMIDES, R—O—CHR′—CH_2Br

Alkyl	R′	Yield, %	B. p., °C.	d^{20}_{20}	Analyses, found	Br, % calcd.
			β-Ethoxy (alkyl) bromides			
n-Butyl[a]	C_2H_5-	62	67 (34 mm.)	1.2312		
n-Amyl[a]	*n*-C_3H_7-	57	82 (34 mm.)	1.1812		
n-Hexyl[a]	*n*-C_4H_9-	81	98–99 (33 mm.)	1.1548		
Isohexyl	iso-C_4H_9-	46	89–92 (38 mm.)	1.1578	37.66	38.23
Isoheptyl[a]	iso-C_5H_{11}	65	106–109 (33 mm.)	1.1209		
			β-Propoxy (alkyl) bromides			
n-Propyl	CH_3-	61	65 (32 mm.)	1.2205	44.17	44.15
n-Butyl	C_2H_5-	73	66 (15 mm.)	1.1803	40.97	40.98
n-Amyl	*n*-C_3H_7-	70	81–82 (13 mm.)	1.1439	38.25	38.23
Isoamyl	iso-C_3H_7-	34	77–78 (14 mm.)	1.1349	37.84	38.23
n-Hexyl	*n*-C_4H_9-	81	92–93 (14 mm.)	1.1226	35.81	35.83
Isoheptyl	iso-C_5H_{11}-	58	112–114 (28 mm.)	1.0872	33.54	33.71
Phenylethyl	C_6H_5	72	123 (12 mm.)	1.2518	33.05	32.88
			β-Butoxy (alkyl) bromides			
Isoheptyl	iso-C_5H_{11}-	65	127–128 (27 mm.)	1.0686	31.88	31.82

[a] Swallen and Boord, THIS JOURNAL, **52**, 655 (1930).

Synthesis of Olefins.—For conversion into the olefin the β-bromo ether was dissolved in approximately two and one-half times its volume of 90% alcohol and placed in a three-necked flask under a spiral condenser. The flask was provided with a mechanical stirrer having a mercury seal. From two to three equivalents of zinc dust were added and the reaction mixture digested at the boiling point for several hours.

The lower bromo ethers decomposed more slowly than those of higher molecular weight. β-Ethoxy-*n*-amyl bromide yielded 60–65% of the crude pentene by treatment for ten to twelve hours, while β-ethoxyisoheptyl bromide gave a yield of 85–90% of isoheptene in five hours. The zinc dust tends to become coated with the basic salt produced. Mechanical stirring serves to obviate this difficulty in part and there is some advantage in adding the zinc portion-wise.

The separation of the olefin from the reaction mixture differed slightly, depending upon its boiling point. In the case of α-pentene the water in the spiral condenser was kept at 40° so that the olefin volatilized from the reaction mixture continuously. The vapors were condensed by leading through a trap immersed in a freezing mixture. In case of the higher olefins the reflux condenser was replaced from time to time by a Hempel column and the product together with a portion of the alcohol distilled off. More alcohol was then added and the digestion continued.

The alcoholic distillates collected in this way were diluted with an equal volume of cold water. The upper layer of olefin was separated, washed with water and dried over calcium chloride. The yields of crude olefins prepared are shown in Table IV.

TABLE IV

α-OLEFINS

β-Alkoxyalkyl bromide	Grams used	Olefin	Yield, %	B. p., °C.	d^{20}_{20}
β-Ethoxy-*n*-amyl	98	$CH_3(CH_2)_2CH{=}CH_2$	65	29.5–31.0	0.6465
β-Propoxy-*n*-amyl	105	$CH_3(CH_2)_2CH{=}CH_2$	57	....	...
β-Ethoxy-*n*-hexyl	150	$CH_3(CH_2)_3CH{=}CH_2$	80	61–64	.6784
β-Ethoxyisohexyl	105	$(CH_3)_2CH{-}CH_2{-}CH{=}CH_2$	60	52.5–54.5	.6718
β-Ethoxyisoheptyl	56	$(CH_3)_2CH(CH_2)_2CH{=}CH_2$	90	84–86	.6956

The products prepared by the above procedure, like those prepared by other methods, do not have as sharp a boiling range as could be desired. Much larger quantities will need to be prepared before they can be obtained in a high degree of purity. Long standing over calcium chloride tends to increase polymerization. Usually about 60% of the crude product distilled with a boiling range of two degrees. Particular difficulty was experienced in the case of iso-α-hexene because of the character of the isobutyl bromide available for the preparation of the corresponding β-bromo ether. The observed boiling points and gravities are also shown in Table IV.

Olefin Dibromides.—From 10 to 15 cc. of each of the olefins described was dissolved in four times its volume of anhydrous ether and cooled in a freezing mixture. An equivalent quantity of bromine was added dropwise with stirring. The bromine was absorbed rapidly and quantitatively. The ether was then evaporated and the dibromo paraffins distilled under diminished pressure. The yields were nearly quantitative.

Analyses for bromine by the Drogin–Rosanoff[18] method were always too low. The error for the lower members was greater than for those of higher molecular weight and in some cases equaled several per cent. Resort to the Carius method showed the compounds to be correctly represented as the dibromides of the olefins indicated in each case. The physical constants and analyses are indicated in Table V.

TABLE V

OLEFIN DIBROMIDES

Formula	B. p., °C.	d^{20}_{20}	Analyses, found	Br, % calcd.
n-C_3H_7CHBr-CH_2Br	84–85 (32 mm.)	1.6525	69.59	69.52
n-C_4H_9CHBr-CH_2Br	103–105 (36 mm.)	1.5632	65.19	65.53
iso-C_4HC_9HBr-CH_2Br	96–99 (38 mm.)	1.5507	65.46	65.53
iso-$C_5H_{11}CHBr$-CH_2Br	110–113 (34 mm.)	1.4913	61.55	61.95

Synthesis of Pentene-1 by the Action of Ethylmagnesium Bromide upon Allyl Bromide.—Twenty-four grams of magnesium was covered with 160 cc. of anhydrous ether and treated with 108 g. of ethyl bromide. To the ether solution of the ethylmagnesium bromide, cooled in ice water, 120 g. of allyl bromide was added during a period of three hours and the reaction mixture allowed to stand overnight. One hundred twenty grams of distillate was collected by heating the reaction mixture over the water-bath and the product so obtained purified by a procedure essentially as described by Norris and Joubert.[7] It was digested at its boiling point with three grams of finely divided metallic sodium for one and three-quarter hours. Three grams more sodium was added and the digestion continued for three hours longer. The product was then removed from the sodium by decantation, 10 g. of magnesium turnings added and the digestion continued for fifteen hours. Distillation yielded 75 cc. of a distillate which was washed five times with 30-cc. portions of a mixture of equal parts of concentrated and 6 N hydrochloric acid. It was then washed ten times with 25-cc. portions of cold water. The moist oily layer, which now weighed 29.5 g., was dried over metallic sodium and fractionated with the following results: 30–33°, 13 g.; 33–36°, 9 g.; 36–41°, 2.1 g.; 41–51°, 1.3 g.

One hundred and eighty cc. of the pentene collected from three condensations in which a total of five moles of the reactants had been used was purified and fractionated using an eight inch Midgley[19] column. A small portion distilling at 28.5° was probably isopentane.[20] The principal fraction totaled 90 cc. and distilled at 29.6–30.8° (mostly

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[18] Drogin and Rosanoff, THIS JOURNAL, **38,** 711 (1916).

[19] Midgley, *Ind. Eng. Chem.* (*Anal. Ed.*), **1,** 86 (1929).

[20] The presence of isopentane is readily accounted for if one assumes that allyl bro-

at 30.1°) under 747 mm. pressure. The residue in the flask still carried a distinct odor of ether. An Engler distillation curve run on the principal fraction showed its purity not yet wholly satisfactory but indicated a boiling point of 30.2° under 747.8 mm. pressure.

Purification of Pentene-1 through its Dibromide.—The condensation of ethylmagnesium bromide with allyl bromide was repeated using one-half molar quantities. Purification was effected by converting the pentene into its dibromide, which was fractionated and the olefin regenerated by the action of zinc dust and alcohol. Sixteen and one-half cc. of bromine was required to saturate the ether solution of the pentene obtained. Fractionation yielded 59 g. of a dibromide boiling at 90–96° under 40 mm. Forty grams of zinc dust was covered with 130 cc. of alcohol and the dibromide added in small portions. The heat developed by the addition of each portion was allowed to subside before a new portion was added. After the addition was completed the reaction mixture was submitted to distillation which began at 27° and was continued up to the boiling point of alcohol. Dilution of the distillate with a large volume of cold water yielded 11.2 g. of the olefin which, after drying over calcium chloride, distilled entirely at 29–31°.

Synthesis of 1,4-Pentadiene

Preparation of 1,4-Pentadiene Tetrabromide, $CH_2Br—CHBr—CH_2—CHBr—CH_2Br$.—A mixture of 180 g. of allyl bromide and 302 g. of α,β-dibromo-ethyl ether was dropped slowly onto 75 g. of magnesium covered with 600 cc. of anhydrous ether. The reaction mixture was vigorously stirred and kept cold in an ice-bath. Although an energetic reaction took place, the mixture did not darken, as is the case when the dibromo ether alone is treated with magnesium. After the reaction was completed the mixture was poured onto cracked ice, the ether layer separated, dried over calcium chloride and distilled. That portion passing over below 60° and containing both the pentadiene and ether was cooled and treated with bromine until no more was absorbed. One hundred and twelve grams (35 cc.) of bromine was required. The ether was removed by distillation and the product allowed to stand. After twenty-four hours the residue had partially crystallized and was filtered by suction. The crystalline product weighed 39 g. and the non crystalline portion 58 g. After washing with cold alcohol the crystalline tetrabromide melted at 78–82°. Recrystallization from alcohol yielded a product melting at 84–87°. Demjanow and Dojarenko[21] give 86° as the melting point of 1,4-pentadiene tetrabromide. Diallyl tetrabromide is described[22] as melting at 63°.

In six runs, involving a total of $9^2/_3$ moles of the dibromo ether, 270 g. of crystalline tetrabromide was obtained. The magnesium consumed varied from 70 to 96% of the theoretical. The bromine absorbed indicated a crude yield of unsaturated product of from 28 to 38% based upon the magnesium consumed. Only 16 to 30% of the tetrabromide obtained could be induced to crystallize.

Anal. Calcd. for $C_5H_6Br_4$: Br, 82.45. Found: Br, 82.73.

Preparation of 1,4-Pentadiene, $CH_2{=}CH—CH_2—CH{=}CH_2$.—One hundred twenty grams of purified crystalline 1,4-pentadiene tetrabromide was placed in a one-liter three-necked flask and covered with 450 cc. of alcohol. The flask was fitted with a mechanical stirrer and a reflux condenser. The top of the reflux was connected by a

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mide, prepared by the action of hydrochromic acid on allyl alcohol, contains a small amount of isopropyl bromide. H. Malbot [*Ann. chim. phys.*, [6] **19**, 355 (1890)] has shown allyl iodide to be easily converted into isopropyl iodide by the action of hydriodic acid.

[21] Demjanow and Dojarenko, *Ber.*, **40**, 2590 (1907).

[22] Tollens and Wagner, *ibid.*, **6**, 589 (1873).

tube leading across and downward through a small coil condenser cooled by ice water into a train of two bottles immersed in a freezing mixture. The tetrabromide was dissolved in the alcohol by boiling. The temperature of the water in the reflux was maintained at 50°, which caused most of the alcohol to be returned but permitted the diolefin vapor to pass through into the receiver. Granular zinc (20-mesh) was then added to the reaction mixture in small portions. A vigorous reaction followed the addition of each portion and would soon have become too vigorous had not the addition been carefully controlled. This process was repeated until all but 2.5 g. of the theoretical 40.6 g. of zinc had been added. A large excess was then added and the reaction completed. About one-third of the alcohol was then distilled into the receiver.

The 130 cc. of liquid condensate was poured into twice its volume of cold water and the colorless, lighter, oily layer separated. The yield of crude diolefin was 9.35 g. or 44.5%. The product was dried and fractionated, yielding 6.2 g. of 1,4-pentadiene boiling at 29-30° (corr.); d^{0}_{25} 0.774.

Five grams of the purified 1,4-pentadiene was dissolved in chloroform and treated dropwise with a solution of bromine in chloroform to complete saturation. The chloroform was evaporated at room temperature and the crystalline product washed twice with cold alcohol and dried. The yield of crude solid was 8 g. or 28%. After two recrystallizations from hot alcohol, 5.2 g. of 1,4-pentadiene tetrabromide was obtained as pure white pearly leaves melting sharply at 86°.

Summary

A nuclear synthesis for α-olefins has been described. The synthesis consists in building up, by well-known reactions, the corresponding β-alkoxyalkyl bromide and the decomposition of this product, in alcoholic solution, by zinc dust. Nine β-bromo ethers of this type are described for the first time.

The method has been applied to the preparation of pentene-1, hexene-1, 4-methylpentene-1 and 5-methylhexene-1. The boiling points of the olefin so prepared agree closely with those given in the literature for the same products as prepared by other low-temperature methods. 1,4-Pentadiene has been prepared by a modification of the same procedure.

A tentative rule has been formulated stating the relationship between the boiling point of an α-olefin and the corresponding saturated hydrocarbon. The usual rule relating boiling points to branching chain structure has been more specifically stated in its application to olefins.

The application of the synthesis to the preparation of other olefins and diolefins is being continued.

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