(7) 4 Kilos Malabar Kino from *Myristica Malabarica:* 3 g. *l*-acacatechin and 11 g. *dl*-acacatechin

(8) 7 Kilos Malabar Kino from *Pterocorpus Marsupium:* 9 g. *l*-acacatechin and 17 g. *dl*-acacatechin

(9) 6 Kilos Australian Kino from *Eucalyptus corymbosa:* 4 g. *l*-acacatechin and 9 g. *dl*-acacatechin

(10) 28 Kilos *Uncaria gambir* leaves: 56 g. *d*-gambir-catechin and 6 g. *dl*-gambir-catechin

(11) 2.8 Kilos *Uncaria acida* leaves: 9 g. *d*-gambir-catechin and 4.5 g. *dl*-gambir-catechin

(12) 11 Kilos Chinese rhubarb: 17 g. *d*-gambir-catechin and 3 g. *dl*-gambir-catechin

(13) 2 Kilos Guarana paste: 5 g. *d*-gambir-catechin and 4 g. *dl*-gambir-catechin

(14) 19 Kilos Kola nuts: 58 g. *d*-gambir-catechin and 8 g. *dl*-gambir-catechin

In conclusion, the authors wish to express their thanks to the Colston Research Society of the University for many generous grants, without which this investigation would not have been possible.

Summary

Eight stereoisomeric catechins have been shown to exist in Nature, of which *d*-acacatechin and *d*-iso-acacatechin have been discovered in the course of the present investigation.

BRISTOL, ENGLAND

NUCLEAR SYNTHESES IN THE OLEFIN SERIES.
II.   1,4-DIOLEFINS[1]

BY BERNARD H. SHOEMAKER[2] AND CECIL E. BOORD

The nuclear synthesis of unsaturated hydrocarbons previously described[3] has been extended to the synthesis of 1,4-diolefins. This extension has been made possible through the preparation of allylmagnesium bromide by the method described by Gilman and McGlumphy.[4]

The addition of an α,β-dibromoalkyl ethyl ether to a slight excess of allylmagnesium bromide in ether solution leads to the formation of an α-allyl-β-bromoalkyl ethyl ether. It has been found in general that β-bromo
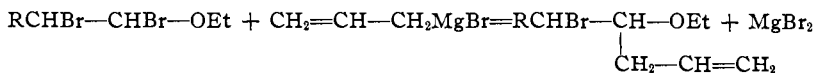
$$RCHBr\text{---}CHBr\text{---}OEt + CH_2\text{==}CH\text{---}CH_2MgBr\text{==}RCHBr\text{---}\underset{\underset{CH_2\text{---}CH\text{==}CH_2}{|}}{CH}\text{---}OEt + MgBr_2$$

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[3] Dykstra, Lewis and Boord, THIS JOURNAL, **52,** 3396 (1930).

[4] Gilman and McGlumphy, *Bull. soc. chim.,* [4] **43,** 1322 (1928).

ethers are most readily purified by steam distillation. This procedure serves to destroy the residual dibromo ether and yields the desired product in a form which may be further purified by direct distillation under diminished pressure. The β-bromo ethers so purified are obtained as water-white limpid liquids and have been kept for many months without apparent deterioration.

The conversion of the β-bromo ethers into the corresponding unsaturated compounds has also been improved. When the ethyl alcohol, as a medium

$$RCHBr—CH—OEt + Zn=R—CH=CH—CH_2—CH=CH_2 + EtOZnBr$$
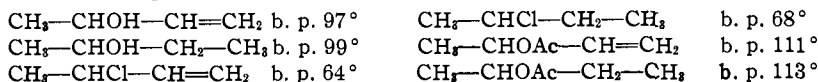$$\text{| } CH_2—CH=CH_2$$
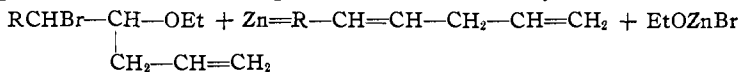
for the decomposition by zinc, is replaced by n-propyl or n-butyl alcohol, both the speed of the reaction and the yield are greatly increased. The increase in reaction velocity is doubtless due in part to the higher boiling point temperatures of the new solvents but it is also due in part to the greater solubility of ethoxyzinc bromide in the new media, so that the surface of the metal is kept clean.

The observations previously made upon the relation of the boiling points of the α-olefins to the corresponding saturated hydrocarbons has been fully confirmed.[5] The data as relating to diolefins having five, six and seven carbon atoms all in a continuous chain are shown in Table I. It will be observed that those dienes having a double bond at each end of the chain boil lower than the corresponding α-olefins. When one of the double bonds is moved away from the end of the chain, the boiling point is raised. As one of the double bonds is moved stepwise toward the one at the opposite end of the chain, the boiling point continues to rise. If both are moved away from the ends of the chain, the boiling point is still higher. The data for the seven carbon atom chains are not complete but in so far as available they stand in good agreement with the above rules.

It has been observed frequently that the tetrabromo paraffins exist in isomeric forms.[6] The same phenomena exist among the polybromo fatty acids.[7] The tetrabromides of the 1,4-diolefins show this same tendency to isomerism. In the case of 1,4-pentadiene the solid phase is obtained in

[5] It has come to our attention that Baudenghien, *Bull. soc. chim. Belg.*, **31**, 160 (1922), has used the same principle in discussing the identity of certain butenols. He cites the following cases

$CH_3—CHOH—CH=CH_2$ b. p. 97°		$CH_3—CHCl—CH_2—CH_3$	b. p. 68°
$CH_3—CHOH—CH_2—CH_3$ b. p. 99°		$CH_3—CHOAc—CH=CH_2$	b. p. 111°
$CH_3—CHCl—CH=CH_2$ b. p. 64°		$CH_3—CHOAc—CH_2—CH_3$	b. p. 113°

So far as we are aware the relationship has not been generalized.

[6] Magnanini, *Gazz. chim. ital.*, **16**, 390–392 (1886); Fournier, *Bull. soc. chim.*, [3] **15**, 403 (1896); Ciamician and Anderlini, *Ber.*, **22**, 2498 (1889); Griner, *Ann. chim.*, [6] **26**, 325 (1892).

[7] Rollett, *Z. physiol. Chem.*, **62**, 410, 421 (1909); Erdmann and Bedford, *Ber.*, **42**, 1324 (1909); Brown and Beal, THIS JOURNAL, **45**, 1301 (1923).

almost quantitative yield. As the number of carbon atoms is increased, the percentage of the solid isomer is decreased.

TABLE I

BOILING POINTS OF THE DIOLEFINS

Hydrocarbons	Boiling points, °C.	Investigator
CH_2=CH—CH_2—CH_2—CH_3	29.5–31	[a] Dykstra, Lewis, Boord
CH_2=CH—CH_2—CH=CH_2	28.5–29.2	Present paper
	25.8–26.2	[b] Kogerman
CH_2=CH—CH=CH—CH_3	43	[c] Auwers and Westermann
CH_2=C=CH—CH_2—CH_3	45	[d] Bouis
CH_3—CH=C=CH—CH_3	49–51	[e] Kukuritschkin
CH_2=CH—CH_2—CH_2—CH_2—CH_3	63.35	[f] van Risseghem
CH_2=CH—CH_2—CH_2—CH=CH_2	59.57	[g] Cortese
CH_2=CH—CH_2—CH=CH—CH_3	64.3–64.6	Present paper
CH_2=CH—CH=CH—CH_2—CH_3	72–74	[h] Fournier
CH_2=C=CH—CH_2—CH_2—CH_3	78	[d] Bouis
CH_3—CH=CH—CH=CH—CH_3	77–78, 81.5–82	[i] Prévost
CH_2=CH—CH_2—CH_2—CH_2—CH_2—CH_3	94.45	[j] Bourguel
CH_2=CH—CH_2—CH=CH—CH_2—CH_3	92–92.3	Present paper
CH_2=C=CH—CH_2—CH_2—CH_2—CH_3	105–6	[d] Bouis
CH_3—CH=CH—CH=CH—CH_2—CH_3	107	[c] Auwers and Westermann

[a] Dykstra, Lewis and Boord, THIS JOURNAL, **52**, 3396 (1930); [b] Kogerman, ibid., **52**, 5060 (1930); [c] Auwers and Westermann, Ber., **54B**, 2998 (1921); [d] Bouis, Ann. chim., **9**, 440 (1928); [e] Kukuritschkin, J. Russ. Phys.-Chem. Soc., Chem. Pt., **35**, 877 (1903); [f] van Risseghem, Bull. soc. chim. Belg., **35**, 328 (1926); [g] Cortese, THIS JOURNAL, **51**, 2268 (1929); [h] Fournier, Bull. soc. chim., [3] **15**, 402 (1896); [i] Prévost, Ann. chim., [10] **10**, 142 (1928). P. believes this diene exists in two forms as indicated; Brühl, Ber., **41**, 3713 (1909), gives 77–78°; Reif, ibid., **41**, 2744 (1908), gives 80–82°; [j] Bourguel, Bull. soc. chim., **41**, 1475 (1927). Soday, in unpublished work done in this Laboratory, finds 94.3°.

Experimental Part

α-Chloroalkyl Ethyl Ethers, R—CHCl—O—C_2H_5.—The method previously described[8] has been improved and extended to the preparation of α-chloropropyl-, and α-chloro-n-butyl ethyl ethers. The darkening of the chloro ether may be avoided if the reaction is conducted so as to avoid undue mixing of the ethereal and aqueous layers. The preparation is best made by placing equimolar quantities of the aldehyde and absolute alcohol in a short-stemmed separatory funnel immersed in a freezing mixture. Hydrogen chloride is then led in in such a manner that it does not pass through the aqueous layer which soon begins to form and violent agitation is avoided. This addition is discontinued when the gain in weight corresponds to a 5% excess over the theoretical value. The aqueous layer is drawn off and the crude chloro ether dried over granular calcium chloride. The excess hydrogen chloride is removed by maintaining the product under diminished pressure, the granules of calcium chloride serving as bumping stones during this process. The product from a well-regulated experiment will be water white. For the purpose of synthesis this crude product is not distilled because of loss by decomposition. The yields of crude chloro ethers are shown in Table II. The physical constants and analyses are for the purified products.

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[8] Swallen and Boord, THIS JOURNAL, **52**, 654 (1930).

TABLE II

α-CHLOROALKYL ETHYL ETHERS, R—CHCl—OC$_2$H$_5$

R	Yield, %	B. p., °C	d_4^{20}	n^{20}	Analyses, Cl, % Calcd.	Found
CH$_3$	78.7[a]	....	..	....	....	....
C$_2$H$_5$	74	34–36 (25 mm.)	0.954	1.4120	28.93	28.59 28.65
n-C$_3$H$_7$	81[b]	49–51 (25 mm.)	.938	1.4168	25.96	24.75 24.68

[a] Swallen and Boord, Ref. 8. [b] James Vaughn (unpublished Master's Thesis, The Ohio State University, 1926) obtained this compound in a yield of 37% of purified product, b. p. 55° (40 mm.); chlorine found, 26.03%.

α,β-Dibromoalkyl Ethyl Ethers, R—CHBr—CHBr—O—C$_2$H$_5$.—In the bromination of the α-chloro ethers it has been found advantageous to avoid aspirating the product with a current of air as previously has been done. A few granules of calcium chloride were added and the reaction mixture maintained under diminished pressure for several hours. The granular calcium chloride serves the dual purpose of drying agent and bumping stones in freeing the product of dissolved hydrogen chloride. The dibromo ethers prepared in this way are pale straw colored liquids. The yields given in Table III are for the crude products. The physical constants and analyses are for products further purified by a single fractionation.

TABLE III

α,β-DIBROMOALKYL ETHYL ETHERS, R—CHBr—CHBr—O—C$_2$H$_5$

R	Yield, %	B. p., °C.	d_4^{20}	n^{20}	Analyses, Br, % Calcd.	Found
H[a]	92–93	....	...	....	...	....
CH$_3$	90–97	79–82 (20 mm.)	1.649	1.5000	64.99	64.88
C$_2$H$_5$	90	99–101 (27 mm.)	1.564	1.4968	61.49	60.69 61.11

[a] Swallen and Boord, Ref. 8; Dykstra, Lewis and Boord, Table I, Ref. a.

Allylmagnesium Bromide, CH$_2$=CH—CH$_2$MgBr.—Seventy-five grams of magnesium turnings was placed in a three-necked flask and covered with 200 cc. of anhydrous ether. The flask was fitted with a mechanical stirrer and a reflux condenser and submerged in an ice-bath. One gram mole of allyl bromide dissolved in 570 cc. of anhydrous ether was added dropwise over a period of eight to nine hours. The formation of the Grignard reagent was started by crushing one or two pieces of magnesium turnings in a test-tube under an ether solution of allyl bromide and adding this to the main portion. The reaction started immediately.

After the addition of allyl bromide was completed, 500 cc. of the ether solution of the Grignard reagent was decanted and the remaining solution replenished by an additional portion of 30–35 g. of magnesium. One-half gram mole of allyl bromide dissolved in 285 cc. of anhydrous ether was then added at the same rate as before. After the addition had been completed, the reaction mixture was allowed to stand for one-half hour. The ether solution was then decanted, care being taken to avoid carrying over any metallic magnesium. The turnings were washed with anhydrous ether and the washings added to the main portion.

The ether solution of allylmagnesium bromide was made up to a definite volume and titrated for reagent content by the method of Gilman, Wilkinson, Fishel and Meyers.[9] The yield of allylmagnesium bromide varied from 70 to 82% and was higher for the larger runs.

α-Allyl-β-bromoalkyl Ethyl Ethers, R—CHBr—CH(C$_3$H$_5$)—O—C$_2$H$_5$.—The ether

[9] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, 45, 150 (1923).

solution of allylmagnesium bromide was placed in a two-liter three-necked flask which had been provided with a mechanical stirrer and reflux condenser. The flask was surrounded by a freezing mixture and the appropriate dibromoalkyl ethyl ether dissolved in an equal volume of anhydrous sulfuric ether added slowly to a slight excess of the Grignard reagent. The condensation proceeded very rapidly. After all of the dibromo ether had been added the flask was allowed to stand at room temperature for one or two hours.

The reaction mixture always separated into two layers, the lower one consisting essentially of magnesium bromide etherate. The entire mass was hydrolyzed by pouring into a beaker of cracked ice and acidifying with dilute hydrochloric acid. The ether layer was separated and slowly distilled on a steam-bath until all of the sulfuric ether had been removed. The residual oil was then distilled with steam. The β-bromo ether, which separated at the bottom of the steam distillate, was drawn off, washed with water and dried over calcium chloride and a small amount of solid sodium hydroxide. The α-allyl-β-bromoalkyl ethyl ethers were finally purified by fractional distillation under diminished pressure.

In all cases a low-boiling portion was obtained which became larger in amount as the molecular weight of the β-bromo ether increased. This proved to be due to the decomposition of the main product by loss of hydrogen bromide and was so pronounced in the case of the branching chained product from isobutyraldehyde that pure α-allyl-β-bromoisobutyl ethyl ether could not be isolated.

The yields, physical constants and analyses of the α-allyl-β-bromoalkyl ethyl ethers prepared are shown in Table IV.

TABLE IV

α-ALLYL-β-BROMOALKYL ETHYL ETHERS, R—CHBr—CH(C$_3$H$_5$)—OC$_2$H$_5$

R	Yield, %	B. p., °C.	d_4^{20}	n^{20}	Analyses, Br, % Calcd.	Found
H	48–50	69–71 (21 mm.)	1.225	1.4592	41.41	41.48
		84–86 (33 mm.)				41.51
CH$_3$	38–43	72–75 (15 mm.)	1.162	1.4592	38.60	36.51 36.71
C$_2$H$_5$	37–45	88–92 (18 mm.)	1.150	1.4606	36.16	34.71 34.36

Preparation of 1,4-Diolefins

It has been found advantageous to substitute the higher boiling propyl and butyl alcohols for ethyl alcohol as the solvent medium in the decomposition of the β-bromo ethers with zinc. The yield of 1,4-pentadiene by the action of zinc dust upon α-allyl-β-bromoethyl ethyl ether in n-butyl alcohol is above 65% in four hours, whereas in ethyl alcohol it is not more than 30% at the end of five days.

1,4-Pentadiene, CH$_2$=CH—CH$_2$—CH=CH$_2$.—One hundred and eight grams of α-allyl-β-bromoethyl ethyl ether was dissolved in 125 cc. of n-butyl alcohol in a one-liter three-necked flask. The flask was provided with a mechanical stirrer and a reflux condenser. The water in the condenser was kept between 35–60° so that the solvent medium was largely condensed and returned to the generating flask while the more volatile 1,4-pentadiene (b. p. 30°) passed through the reflux into a second condensing system and was collected in a receiver immersed in an ice-bath. One hundred grams of zinc dust was added portion-wise as the reaction proceeded. The speed of the reaction was so regulated that the pentadiene distilled over at approximately one drop per second as a maximum. In four hours 25 g. or 65.8% of the theoretical yield was obtained. After drying over calcium chloride it was distilled twice from metallic sodium

to remove any traces of butyl alcohol. The yield of purified product was 20 g. or 52.6%. The boiling range of the major portion was 28.5–29.2° (742 mm.).[9a]

1,4-Hexadiene, $CH_2\!\!=\!\!CH\!\!-\!\!CH_2\!\!-\!\!CH\!\!=\!\!CH\!\!-\!\!CH_3$.—One hundred ten grams of α-allyl-β-bromopropyl ethyl ether, 225 cc. of n-propyl alcohol and 100 g. of zinc dust were refluxed for fifteen hours. Thirty-eight grams of crude distillate was collected and washed five times with one-half its volume of ice cold water. The product was dried over calcium chloride and distilled twice from metallic sodium to remove absorbed alcohol. The purified product weighed 29.4 g., had a boiling range of 63–64.8° and represented a 67.4% yield. The major portion distilled at 64.3–64.6° under 745 mm. pressure.

This boiling point is in good agreement with 64–66° as given by Griner[10] for a compound prepared by the action of hydriodic acid upon diallyl and subsequent decomposition of the iodide thus obtained by alcoholic potassium hydroxide. Merling[11] has also described a product as 1,4-hexadiene. This product was obtained by heating pentenyltrimethylammonium hydroxide in an oil-bath to 160° or in better yield by heating the same quaternary ammonium hydroxide with water in a sealed tube at 180°. Since the boiling point of his diene (80–83°) was too high for diallyl, which he had expected to obtain, he has offered a reaction mechanism to show isomerization to 1,4-hexadiene. In the light of the present work and that of Griner it would seem probable that the isomerization at the high temperatures used was more deep-seated than Merling had supposed.

1,4-Heptadiene, $CH_2\!\!=\!\!CH\!\!-\!\!CH_2\!\!-\!\!CH\!\!=\!\!CH\!\!-\!\!CH_2\!\!-\!\!CH_3$.—Since the boiling point of this diolefin lies close to that of n-propyl alcohol, no attempt was made to separate the product from the reaction mixture as formed. After the refluxing had been continued for several hours, the condenser was replaced by a distilling tube and the diene together with a portion of propyl alcohol distilled off. The mixture began distilling at 83°, the temperature gradually rising to 94° when the distillation was stopped. This process of refluxing and distilling was continued until no more of the diolefin could be separated from the distillate upon dilution with water. One hundred grams of α-allyl-β-bromobutyl ethyl ether, 225 cc. of n-propyl alcohol and 100 g. of zinc dust yielded 37 g. of crude 1,4-heptadiene. After purification, as described above, there remained 23 g. of product having a boiling range of 90.2–92.6° of which 18 g. distilled at 92.0–92.3° at 755 mm.

TABLE V

1,4-DIOLEFINS

Diene	d_4^{20}	n^{20}	Boiling point. °C. Observed	Literature
1,4-Penta	0.672	1.3880	28.5–29.2 (742 mm.)	29.5–31[a]
1,4-Hexa	.6996	1.4162	64.3–64.6 (745 mm.)	64–66[b]
1,4-Hepta	.7176	1.4202	92.0–92.3 (755 mm.)	

[a] Dykstra, Lewis and Boord, Table I, Ref. a.   [b] Griner, Ref. 6.

[9a] While this paper was being written for publication, an article by Kogerman on the "Synthesis of 1,4-Pentadiene," THIS JOURNAL, **52,** 5060 (1930) has appeared. The author was unaware of our previous communication, *ibid.*, **52,** 3396 (1930), in which the same compound is described. Kogerman prepared 1,4-pentadiene in 15% yield by the action of allylmagnesium bromide on vinyl bromide. The work was evidently done with great care and the product obtained in almost exceptional purity. He gives the following physical constants: b. p. 25.8–26.2° at 756 mm.; d_4^{20} 0.6594; n_D^{20} 1.3883; mol. refraction calcd., 24.26; found, 24.26.

[10] Griner, *Ann. chim.*, [6] **26,** 332 (1892).

[11] Merling, *Ann.*, **264,** 345 (1891).

Diolefin Tetrabromides

The tetrabromides of the diolefins were prepared by slowly adding bromine to a well-cooled solution of the hydrocarbon in chloroform. The reaction proceeded quite definitely in two steps; bromine was absorbed rapidly until approximately one-half of the required amount had been added; the remainder was absorbed more slowly. No attempt was made to isolate the intermediate diolefin dibromides.

1,4-Pentadiene Tetrabromide, CH_2Br—$CHBr$—CH_2—$CHBr$—CH_2Br.—Eighteen grams of 1,4-pentadiene was dissolved in five times its volume of chloroform and the solution cooled in a freezing mixture. Bromine was added drop by drop until the solution maintained a permanent red coloration. The reaction mixture was placed under diminished pressure and the excess of bromine removed. Upon evaporation of the solvent the tetrabromide almost wholly solidified to a crystalline mass. After a third recrystallization from absolute alcohol, the product melted at 85.5 to 86°. The yield of purified product was 65%.

The oily residue from the crystals was filtered and distilled under diminished pressure. Analysis showed this liquid phase to be low in bromine.

1,4-Hexadiene Tetrabromide, CH_3—$CHBr$—$CHBr$—CH_2—$CHBr$—CH_2Br.— More difficulty was encountered in crystallizing 1,4-hexadiene tetrabromide. The viscous oil, free from chloroform, failed to crystallize at room temperature or in the ice-bath. Crystals were finally obtained by dissolving the liquid tetrabromide in absolute alcohol and chilling the solution in a bath of liquid ammonia. The crystals thus obtained were used to seed the remaining solutions cooled in a bath of ice and salt. After recrystallization, 8 g. of solid tetrabromide, m. p. 63.5–64°, was obtained together with 60 g. of the liquid isomer. The liquid tetrabromide was freed from volatile impurities by placing in a vacuum for four hours at a temperature of 40° and analyzing without further purification.

Griner[6] has described 1,4-hexadiene tetrabromide in three forms; the α-form melted at 182.3°, the β-form melted at 63–64° and the γ-form was a liquid which could not be distilled. The α-form was not obtained in the present work. Merling[11] gives the melting point of 1,4-hexadiene tetrabromide as 160–162° but his diolefin boiled 20° higher than the product herein described.

1,4-Heptadiene Tetrabromide, CH_3—CH_2—$CHBr$—$CHBr$—CH_2—$CHBr$— CH_2Br.—All attempts to crystallize this tetrabromide failed. When chilled in a liquid ammonia bath it solidified to a glass which melted completely upon removing from the bath. After volatile impurities had been removed in a vacuum, the product was analyzed without further purification. The yield was 97% on the basis of diolefin used. The physical characteristics and analyses of these 1,2,4,5-tetrabromo paraffins are shown in Table VI.

TABLE VI

1,4-DIOLEFIN TETRABROMIDES, CH_2Br—$CHBr$—CH_2—$CHBr$—$CHBr$—R

1,4-Diene	Physical state	M. p., °C.	d_4^{20}	n^{20}	Analysis, Br, % Calcd.	Found
Penta	Solid	85.5–86[a]	...	....	82.44	82.58 82.56
	Liquid	......	...	....	82.44	79.16
Hexa	Solid	63.5–64[b]	...	....	79.57	79.76 79.67
	Liquid	......	2.207	1.5833	79.57	79.36 79.31
Hepta	Liquid	......	2.091	1.5734	76.90	76.71 76.61

[a] Demjanow and Dojarenko, *Ber.*, **40**, 2590 (1907), give 86°; Dykstra, Lewis and Boord, Table I, Ref. a, also give 86°. [b] Griner, Ref. 6, gives 64–66°.

Summary

By the use of allylmagnesium bromide the β-bromo ether synthesis of olefins has been extended to the preparation of 1,4-diolefins. 1,4-Pentadiene, 1,4-hexadiene and 1,4-heptadiene and the corresponding α-allyl-β-bromoalkyl ethers have been described.

The rule that unsaturated compounds with a double bond in the alpha position boil lower than the corresponding saturated hydrocarbons has been confirmed. It has been further shown that in any given family the continuous chain diolefins form a definite series with gradually increasing boiling points depending upon the relative position of the double bonds.

The 1,2,4,5-tetrabromo paraffins corresponding to the diolefins described have been prepared and found to show evidences of isomerism analogous to other polybromo aliphatic derivatives.

COLUMBUS, OHIO

THE OXIDATION OF METHANOL WITH AIR OVER IRON, MOLYBDENUM, AND IRON-MOLYBDENUM OXIDES

BY HOMER ADKINS AND WESLEY R. PETERSON

The oxidation of methanol with air over various metal and oxide catalysts at 300 to 700° results in the formation of varying amounts of formaldehyde, carbon monoxide and carbon dioxide. Sabatier and more recently Lowdermilk and Day have given a review of the literature on this oxidation to which little need be added at this time.[1]

In 1926 a catalyst containing equal amounts of iron and molybdenum was found to be very efficient for the oxidation of methanol to formaldehyde.[2] The investigation described in this paper was initiated in order to correlate the characteristics of the iron–molybdenum catalyst with those of the catalyst containing only iron or molybdenum, with the hope of throwing some light upon the mechanism of the oxidation.

Catalysts. Molybdenum Oxide.—Five grams of ammonium molybdate and 4.5 g. of malic acid were dissolved in water and made ammoniacal with ammonium hydroxide.

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[1] Sabatier–Reid, "Catalysis in Organic Chemistry," Van Nostrand Company, New York, 1922, pp. 90–97; Lowdermilk and Day, THIS JOURNAL, 52, 3535 (1930).

[2] Homer Adkins and Virgil E. Meharg, in an application for a U. S. Patent (1927) assigned to the Bakelite Corporation. The authors of the present paper are indebted to Mr. Meharg and the Bakelite Corporation for the design of the very efficient washing tower and for the design and construction of the catalyst chamber, which were used in this investigation. The senior author is also grateful to Mr. Meharg for many pleasant associations and very valuable and willing coöperation while the former was temporarily employed by the Bakelite Corporation during the summer of 1926.