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STUDIES ON POLYMERIZATION AND RING FORMATION. VII. NORMAL PARAFFIN HYDROCARBONS OF HIGH MOLECULAR WEIGHT PREPARED BY THE ACTION OF SODIUM ON DECAMETHYLENE BROMIDE

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No rationally synthetic and practical methods for the preparation of giant individuals of the simpler homologous series are available, and one of the objects of the experiments here reported was to explore the possibilities of bifunctional Wurtz reactions as a means of access to this realm.

The first step in simple Wurtz reactions is the formation of the corresponding sodium alkyl, RNa.[1] This normally couples with the halide, forming the hydrocarbon R-R, but it may react in other ways and yield by-products. Sodium ethide reacts with diethyl ether

$$C_2H_5Na + (C_2H_5)_2O = C_2H_6 + C_2H_5ONa + C_2H_4{}^{2}$$

and one may expect the formation of considerable amounts of the hydrocarbon RH when the Wurtz reaction is carried out in that solvent.

The experiments presently described are concerned with the action of sodium on decamethylene bromide in ethereal solution, and the normal course of this reaction including that due to the participation of the solvent (but ignoring for the moment the possibility of intramolecular reaction) may be formulated as follows

$$\begin{array}{l}
Br(CH_2)_{10}Br + 2Na = Br(CH_2)_{10}Na + NaBr \\
Br(CH_2)_{10}Na + (C_2H_5)_2O = H(CH_2)_{10}Br + C_2H_5ONa + C_2H_4 \\
Br(CH_2)_{10}Na + Br(CH_2)_{10}Br = Br(CH_2)_{20}Br + NaBr \\
H(CH_2)_{10}Br + 2Na = H(CH_2)_{10}Na + NaBr \\
H(CH_2)_{10}Na + (C_2H_5)_2O = H(CH_2)_{10}H + C_2H_5ONa + C_2H_4 \\
H(CH_2)_{10}Na + H(CH_2)_{10}Br = H(CH_2)_{20}H + NaBr \\
H(CH_2)_{10}Na + Br(CH_2)_{10}Br = H(CH_2)_{20}Br + NaBr \\
H(CH_2)_{10}Na + H(CH_2)_{20}Br = H(CH_2)_{30}H + NaBr \\
H(CH_2)_{10}Na + Br(CH_2)_{20}Br = H(CH_2)_{30}Br + NaBr \\
H(CH_2)_{30}Br + 2Na = H(CH_2)_{30}Na + NaBr \\
H(CH_2)_{30}Na + Br(CH_2)_{20}Br = H(CH_2)_{50}Br + NaBr, \text{ etc.}
\end{array}$$

The product will be composed of individuals of the general formula $H[(CH_2)_{10}]_xH$ and possibly of similar chains terminated at one or both ends by bromine atoms. The length of these chains will be determined by the relative rates of reaction of the sodium compounds with the solvent and with the halides. Solubility effects may also come into play.

The suitability of this reaction as a source of straight chain hydrocarbons will depend upon the extent to which it is possible to avoid undesirable

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[1] Schorigin, *Ber.*, **40**, 3111 (1907); **43**, 1931 (1910); Schlubach and Goes, *ibid.*, **55**, 2889 (1922); Ziegler and Colonius, *Ann.*, **479**, 135 (1930).

[2] Schorigin, Ref. 1; *Ber.*, **41**, 2723 (1908).

side reactions, and some indications on this point may be had from the known behavior of simple halides. Sodium and *n*-heptyl bromide at the boiling temperature give tetradecane, 67%; heptane, 9%; heptene, 3%; heneicosane, 3%; hydrocarbons of higher molecular weight, some.[3] Sodium and butyl bromide in ether under specified conditions give *n*-octane, 68%; butane ?, ?%; butene, *ca.* 1.5%; dodecane, *ca.* 0.15%; hexadecane, *ca.* 0.05%.[4] In both these typical cases the principal by-product is probably the hydrocarbon RH. In the reaction of the dihalide, this type of by-product would be identical with one of the normal reaction products. The higher hydrocarbons from butyl bromide and from heptyl bromide are probably not straight chains, and the formation of analogous products from the dihalide would be definitely pernicious because of the difficulty of separating isomeric individuals of high molecular weight. The quoted data on butyl bromide indicate however that in simple Wurtz reactions in ether not more than traces of these higher by-products need be formed.

The action of sodium wire on decamethylene bromide in absolute ether has been studied by Franke and Kienberger.[5] The reaction proceeded smoothly to completion, and the products isolated were: *n*-decane, 34%; C_{20} hydrocarbon, 30%; a small amount of C_{40} hydrocarbon; and a considerable amount of solid hydrocarbon of higher molecular weight. All of these products were free of halogen. The melting point of the C_{20} hydrocarbon identifies it as *n*-eicosane. The formation of large amounts of *n*-decane apparently puzzled Franke and Kienberger, and they repeated their experiments with elaborate precautions to exclude water and alcohol from the solvent and the halide. The results were the same. *n*-Decane and *n*-eicosane are, however, strictly normal products of the reaction as it has been formulated above. The fact that Franke and Kienberger could find neither decene nor cyclodecane in the products is worthy of note, for any side reaction would almost certainly be accompanied by the formation of some decene, and any intramolecular reaction by the formation of some cyclodecane. These data indicate that the course of this reaction is, at least for the most part, strictly normal and exclusively intermolecular. The major part of the product is composed of relatively short chains, but this is a matter which may be expected to be susceptible of some control by changes in the experimental conditions, and, as it appears to be in fact, especially by increase in the surface of the sodium.

We had already treated decamethylene bromide in ether with finely divided sodium with stirring before Franke and Kienberger's paper had come to our attention. The product, obtained in good yield, was an ether-in-

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[3] Bachmann and Clarke, THIS JOURNAL, **49**, 2089 (1927).

[4] Lewis, Hendricks and Yohe, *ibid.*, **50**, 1993 (1928).

[5] Franke and Kienberger, *Monatsh.*, **33**, 1189 (1912).

soluble solid, and no material boiling as low as *n*-decane was present. This product, by extraction and crystallization, was separated into $C_{20}H_{42}$, $C_{30}H_{62}$ and $C_{40}H_{82}$, each fairly pure, representing together about 25% of the total, and a higher fraction, m. p. 108–112°, representing about 75% of the total. This contained 1.39% organic halogen, from which it was freed by heating and stirring it with a small amount of molten sodium in boiling butyl ether. The apparent molecular weight of the resulting hydrocarbon was about 1000. No individuals could be isolated from it by repeated fractional crystallization, and it could not be distilled at 0.1 mm. pressure. It was finally separated into a series of individuals by distillation in the molecular still and by crystallization of the distillates.

Preparation of the Hydrocarbon Mixture.—In a 500-cc. flask provided with a reflux condenser and a mercury-sealed mechanical stirrer, 95 g. (1.52 atoms) of sodium was pulverized under hot xylene. The xylene was removed and replaced by absolute ether, and then 75 g. (0.25 mole) of decamethylene bromide was added. The reaction mixture was stirred continuously. It soon developed a deep blue color. It was gently heated for one hour and then allowed to boil without external heating for two and one-half hours. Finally it was heated for two and one-half hours more and then allowed to stand overnight. The excess sodium in the thick mass was decomposed by alcohol, a large volume of water was added, and the mixture was filtered with suction. The only material found in the ethereal layer of the filtrate was 0.5 cc. of an oil boiling at 240–330°. The soft white residue on the funnel liquefied almost completely on being stirred with boiling water and solidified to a crystalline mass on cooling. It weighed 30.5 g. (87.1% calculated as CH_2). It melted from 85 to 100° and contained bromine (found, 2.17, 2.27%). This solid was heated and vigorously stirred for five hours with 7 g. of molten sodium in boiling butyl ether. The excess sodium was decomposed by alcohol, a large volume of water was added, and the mixture was filtered. The solid residue on the funnel was washed with boiling water and dried. It weighed 21 g. It was free of halogen and melted from 87 to 105°. This is the material which was submitted to fractionation in the molecular still. After the butyl ether had been removed from the non-aqueous layer of the distillate, there remained 6 g. of a soft waxy solid melting at 48–54°.

Separation of the Hydrocarbon Mixture.—Eight grams of the solid hydrocarbon, m. p. 87–105°, described above was heated in a small molecular still[6] provided with a water-cooled condenser and a trap cooled with liquid air. The pressure in the system was continually maintained below 10^{-5} mm. Fractions were collected as follows.

Temp. of bath, °C.	Wt. of distillate, g.	M. p. of distillate, °C.
130	0.7	35 - 55
150–160	.27	60 - 75
150–160	.15	60 - 78
150–160	.20	77 - 79
160	.12	78 - 81
180	.20	79 - 84
190	.19	87 - 89

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[6] Washburn, *Bur. Standards J. Research*, **2**, 476 (1929).

Temp. of bath, °C.	Wt. of distillate, g.	M. p. of distillate, °C.
195	.08	87 - 91
195	.10	90 - 90.5
200–220	.52	90.5- 92
250	.31	94.5- 97
250	.11	96 - 98
250	.20	97 - 99.5
250	.10	98 -100.5
250	.05	99 -101
250	.08	99 -102
300	.47	103 -105
300	.17	103 -106.5
Total	4.02	
Residue	3.16	
Loss	0.82	

The loss is due to the impossibility of quantitatively removing the distillate from the condenser. In this distillation the average area of the evaporating surface was about 18 sq. cm. About twenty hours was required for the collection of each of the above listed fractions. When the temperature of the heating bath was raised above 300° with the view of distilling the residue, the pressure rose and no distillation could be effected.

The distillates were grouped together into eight fractions and redistilled. The rate of distillation from these partially purified materials was very much higher than from the initial mixture. The distillates were crystallized to constant melting points. The properties of all the fractions thus obtained are indicated in Table I.

TABLE I

INDIVIDUAL HYDROCARBONS

Hydrocarbon	M. p. found, °C.	Solvent used for crystallization	Distn. temp., °C.	Anal. calcd. C	Anal. calcd. H	Anal. found C	Anal. found H
$C_{20}H_{42}$	35 - 35.6	Abs. EtOH	60°	85.00	15.00	85.45	15.03
$C_{30}H_{62}$	65 - 66	Abs. EtOH + Et_2O	100	85.21	14.79	85.28	14.45
$C_{40}H_{82}$	80.5- 81	Ethylene chloride	150	85.31	14.69	85.59	14.74
$C_{50}H_{102}$	91.9- 92.3	Ligroin + petroleum ether	200	85.37	14.63	85.34	14.53
$C_{60}H_{122}$	98.5- 99.3	Butyl acetate	250	85.41	14.59	85.66	14.34
$C_{70}H_{142}$	105 -105.5	Butyl acetate	300	85.44	14.56	85.50	14.58
Soluble residue	110 -114	Butyl acetate	Not distillable				

Identity and Properties of the Hydrocarbons.—The melting points 36.7°[7] and 65.6–66°,[8] respectively, have been assigned to *n*-eicosane and

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[7] Krafft, *Ber.*, 19, 2220 (1886). The C_{20} hydrocarbon of Franke and Kienberger (Ref. 5) which melted at 36° was unquestionably *n*-eicosane; and their C_{40} hydrocarbon, which melted at 72°, was probably a mixture of *n*-triacontane and *n*-tetracontane.

[8] Gascard, *Ann. chim.*, [9] 15, 332 (1921); Peterson, *Ber.*, 12, 741 (1879).

n-triacontane, and these values are in good agreement with our observations. The other four hydrocarbons listed in Table I are all new, and the last one stands six atoms above any paraffin previously described. Several intermediate members of this same series have been described, however, and from the available data it is possible to construct a smooth curve of melting points covering the range C_{18}–C_{70}. The usefulness of such a curve in estimating the most probable values for individual hydrocarbons has already been emphasized,[9] and in the curve presented in Fig. 1 the crosses are Hildebrand and Wachter's estimates of the best values for hydrocarbons in the range C_{19}–C_{36}. We have used a method of plotting similar to that suggested by Austin[10] and have included the values for the three previously known hydrocarbons above $C_{36}H_{74}$. These are $C_{54}H_{110}$, $C_{62}H_{126}$ and $C_{64}H_{130}$, all described by Gascard.[8] Our data and those of Gascard fall very close to the same smooth curve which fits the best data for the lower hydrocarbons, and this fact incidentally affords confirmation of Hildebrand and Wachter's contention that the melting points accepted by the "International Critical Tables" for some of the hydrocarbons in the range C_{24} to C_{32} are much too high. Hell and Haegele described dimyricyl in 1889[11] and ascribed to it the formula $C_{60}H_{122}$. This ascription acquired the sanction of recognition by Beilstein (third and fourth editions) and remained unquestioned until evidence that the myricyl radical contains 31 carbon atoms appeared. In 1921 Gascard[8] concluded that Hell and Haegele's hydrocarbon was $C_{62}H_{124}$ and that hexacontane had never been prepared. Our data confirm this

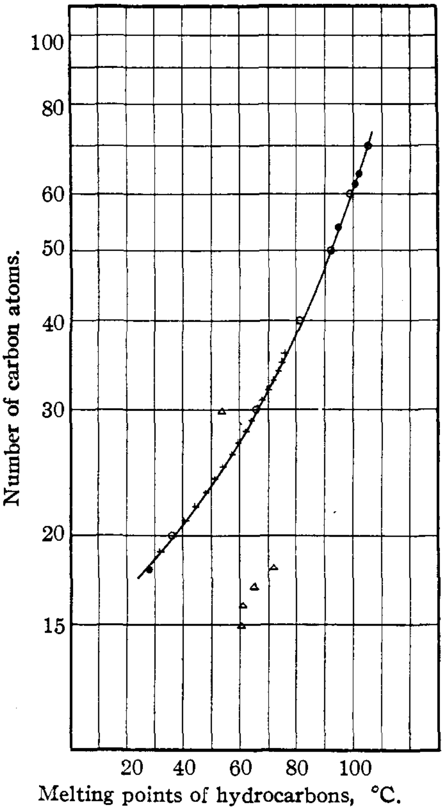

Fig. 1.—Normal paraffins: ●, Gascard, *Ann. chim.*, [9] **15**, 332 (1921); +, Hildebrand and Wachter, THIS JOURNAL, **51**, 2487 (1929); ○, new data. Cyclopolymethylenes: △, Ruzicka and co-workers. *Helv. Chim. Acta*, **9**, 499 (1926); **11**, 496 (1928).

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[9] Hildebrand and Wachter, THIS JOURNAL, [9] **51**, 2487 (1929).

[10] Austin, *ibid.*, **52**, 1049 (1930).

[11] Hell and Haegele, *Ber.*, **22**, 502 (1889).

conclusion. Hexacontane melts at 98.5 to 99.3°, while the observed melting points ascribed to dimyricyl have ranged from 100.5–102°.

Independent proof of the identity of the six hydrocarbons is furnished by x-ray diffraction patterns which have been obtained by Dr. A. W. Kenney and will be described in a separate publication.

Melting point data are available for only five cyclic polymethylenes above C_{10}. These fragmentary data do not fall on any smooth curve (see Fig. 1), but they are all widely enough separated from the data for the normal paraffins to provide additional assurance that none of our paraffin compounds are cyclic.

Under the heading distillation temperature in Table I are listed the minimum bath temperatures required to effect evaporation at a moderate rate in the molecular still. These temperatures are quite characteristic since they are, in each case, only a few degrees above the temperatures at which no distillation occurs. Using the Langmuir formula[6] it is possible to make a rough calculation of the order of magnitude of the vapor pressures of these hydrocarbons from the minimum distillation temperatures. Such calculations indicate a value less than 0.01 mm. for heptacontane at 300° and a value less than 1 mm. for triacontane at 100°. Heptacontane has a molecular weight of 983, and it is probable that no organic compound of much higher molecular weight than this can ever be distilled under any experimental conditions however favorable. The residue remaining from the removal of the heptacontane undoubtedly contained some octacontane, but none of this distilled out at a bath temperature of 300° and when the temperature was raised higher than this, decomposition set in. This experimental result agrees remarkably well with the inferences to be drawn from the data presented by Meyer and Dunkel.[12] From these data one can calculate that the molecular cohesion of heptacontane will be about 71,000 calories and that of octacontane about 81,000 calories. Since the heat of separation of the carbon–carbon bond is about 75,000 calories, it should be possible to distil the first of these compounds, but not the second. Saturated paraffins have, in general, a lower molecular cohesion for a given molecular weight than any other types of compounds, and hence the limit of distillability will be found at a lower molecular weight for other compounds than hydrocarbons. These results are also in agreement with data of a different kind presented by Burch[13] who, by distilling a Pennsylvania petroleum in a molecular still, obtained as the highest distillable fraction a material having an apparent average molecular weight of 801 and a residue of apparent molecular weight of 1550.

The physical properties of *n*-heptacontane are similar to those ascribed to dohexacontane and tetrahexacontane. It is very slightly soluble in

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[12] Meyer, *Naturw.*, **16**, 781 (1928); Dunkel, *Z. physik. Chem.*, **138**, 42 (1928).

[13] Burch, *Proc. Roy. Soc.* (London), **123**, 271 (1929).

boiling alcohol, ether or petroleum ether, but crystallizes well in the form of minute needles from hot butyl acetate or benzene. It dries to a starch-like powder which has a great tendency to become electrified.

It was hoped that it might be possible to isolate hydrocarbons much higher than heptacontane, since information concerning simple individuals of very high molecular weight would be of great importance to the study of macromolecular materials generally, but there seems little probability of achieving this result without some change in method or advance in technique. The residue from which the *n*-heptacontane was distilled is a mixture which undoubtedly contains *n*-octacontane, *n*-nonacontane, *n*-decacontane and still higher hydrocarbons. It is readily soluble in hot butyl acetate (except for a trace of insoluble and infusible material), and it separates as a powder melting at 110–114°. Its apparent average molecular weight in boiling benzene is about 1300. (Calcd. for $C_{90}H_{182}$, 1263.) By extraction with hot ethylene chloride, it was separated into fractions melting at 100–107°, 106–111° and 110–114°. In a sense this mixture is a polymeric homologous series, but its solubility is much lower than that of such supposedly analogous series of higher molecular weight as polystyrene and hydro-rubber. It resembles a probably similar but more complex mixture of hydrocarbons obtained by Fischer and Tropsch by the catalytic hydrogenation of carbon monoxide.[14]

There is one point bearing on the behavior of highly polymeric materials which is capable of a rough preliminary test with the series of hydrocarbons described above. It has been suggested[15] that the apparent decrease of molecular weight (decrease of viscosity, etc.), which is observed when rubber and other very high polymers are gently heated or treated with certain mild chemical agents or subjected to mechanical stresses, is real and is due to the fact that the thermal stability of molecules decreases continuously with increasing size, and in these materials has reached so low a value that cracking occurs at slightly above room temperature. Samples of each of the hydrocarbons from C_{30} to C_{70} were sealed off in small bulbs under nitrogen and heated side by side in a metal-bath. After five minutes at 400° all the melting points were unchanged. After five minutes at 410° the melting point of C_{70} was lowered from 106–107° to 104–105°. The melt, moreover, was not clear as before but turbid. The turbidity disappeared rather sharply at 110°—like a liquid crystal. The melting points of the other hydrocarbons were substantially unchanged, but, except for C_{30}, they all gave hazy melts which cleared up only at temperatures somewhat above their true melting points. After five minutes more at 420° all the melting points had become lower (that of C_{70} most) and there was some coloration. The C_{30} was white, the C_{40} was cream-colored, and the higher hydrocarbons

[14] Fischer and Tropsch, *Brennstoff-Chemie*, **8**, 165 (1927).

[15] Staudinger, *Ber.*, **59**, 3037 (1926).

in regular order were increasingly darker. When the tubes were finally opened after five minutes more at each of the temperatures 430, 450 and 470°, they were found to contain considerable gas—most above the C_{70} and least above the C_{30}. Thus, the decrease in thermal stability with increasing molecular weight which is so marked in passing from methane (*ca.* 700°)[16] to ethane (*ca.* 550°),[17] and from ethane to hexadecane (*ca.* 470°)[18] is still detectable in going from triacontane to heptacontane, but it has already fallen to such a small value that it would be somewhat unsafe to infer that a paraffin hydrocarbon of molecular weight 200,000 or even greater might not persist at room temperature.

Mechanism of the Action of Sodium on Decamethylene Bromide.—It has already been pointed out that all the observed products of this reaction are accounted for by assuming replacement of the bromine atoms of the halide by sodium, and the subsequent coupling of this with other molecules of the halide, or its reaction with the solvent. The absence of cyclic hydrocarbons is not surprising since, although the higher cycloparaffins are no less stable than cyclohexane,[19] the formation of large rings in bifunctional reactions occurs only under very exceptional conditions.[20] In the formation of esters from ω-hydroxy acids, amides from amino acids, and anhydrides from dibasic acids, intramolecular reaction occurs exclusively only if there is a possibility of forming a 5- or a 6-membered ring. The behavior of alkylene halides toward metals however is peculiar in that there seems to be little tendency toward intramolecular reaction even when a 5- or a 6-membered ring might be formed. Thus the action of magnesium on alkylene halides leads to considerable coupling, but even from pentamethylene halides no cyclic hydrocarbon is formed.[21] This suggests that the coupling perhaps occurs largely at the metal surface where the atoms at the ends of the chains may be fixed by forces of adsorption and their freedom of intramolecular approach hindered.

Our main objective in the experiments described above was to prepare normal paraffins of very high molecular weight, and we made a number of attempts to adjust the experimental conditions so as to increase the length of the reaction chains. We treated decamethylene bromide with molten sodium in boiling butyl ether, with liquid sodium–potassium alloy in ethyl ether, with molten sodium in boiling octane and with finely divided sodium in the absence of a solvent. There was no evidence of the formation of considerable amounts of paraffins higher than C_{100} in any of these experi-

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[16] Bone and Wheeler, *J. Chem. Soc.*, 81, 542 (1902).

[17] Williams-Gardner, *Fuel Science Practice*, 4, 430 (1925).

[18] Gault and Hessel, *Ann. chim.*, [10] 2, 319 (1924).

[19] Ruzicka and co-workers, *Helv. Chim. Acta*, 9, 499 (1926); 11, 496 (1928).

[20] Carothers, THIS JOURNAL, 51, 2548 (1929); and subsequent papers of this series.

[21] Zappi, *Bull. soc. chim.*, [4] 19, 249 (1916); v. Braun and Sobecki, *Ber.*, 44, 1918 (1911).

ments. We also prepared decamethylene dimagnesium bromide and treated it with cupric chloride in the expectation that products of the formula $BrMg[(CH_2)_{10}]_xMgBr$ would be formed. The chief product (71%), however, after the addition of water, was a volatile liquid apparently chiefly composed of decane and decene. The amount of higher boiling material (20%) did not exceed that which would arise from the coupling products usually produced in the formation of such reagents as decamethylene dimagnesium bromide.[21]

Preparation of Decamethylene Bromide.—The preparation, in good yields, of a whole series of polymethylene bromides from the glycols via the esters of the corresponding dibasic acids has been described by Chuit[22] but without great experimental detail. We first attempted to reduce ethyl sebacate by Levene and A len's modification[23] of the original Bouveault procedure.[24] In this modification, which has given good results in the reduction of esters of monobasic acids, the sodium is first granulated by stirring in hot toluene, and the reaction mixture is vigorously stirred during the addition of the alcohol–ester mixture. This procedure gave very poor yields of decamethylene glycol; the yields were increased by diminishing the speed of stirring and became quite good when the stirring was omitted altogether. The procedure finally adopted was almost identical with that of Bouveault, and the details are given below.

A condenser having a length of 2 meters and an inside diameter of about 2.5 cm. is connected with the side neck of a 5-liter two-necked round-bottomed flask, and the central neck of the flask is provided with a 1-liter dropping funnel. One hundred and fifteen grams (5 atoms) of sodium in a single piece or in two or three large pieces is placed in the flask. One hundred and twenty-nine grams (0.5 mole) of ethyl sebacate is dissolved in one liter of thoroughly dried absolute ethyl alcohol and poured into the dropping funnel. One hundred and fifty to two hundred cubic centimeters of the alcohol–ester mixture is allowed to fall onto the sodium at once. After two or three minutes the reaction becomes vigorous and the sodium melts. As soon as the sodium has melted another portion (about 100 cc.) of the alcohol–ester mixture is suddenly added. This causes the molten sodium to break up into fine particles, and the reaction becomes much more vigorous. The rest of the alcohol–ester mixture is then added as rapidly as possible (five to six minutes). As soon as the vigor of the reaction has somewhat subsided, the flask is heated by an oil-bath to 110-115° until most of the sodium has dissolved. The ethyl alcohol is then removed from the reaction mixture by steam distillation, and the glycol is removed from the residue by extended (about seventy-two hours) continuous extraction with ether. The glycol is purified by distillation. The combined yield from nine such runs was 593 g. or 75% of the theoretical.

Continuous ether extraction as a means of isolating glycols produced by the reduction of esters has been successfully used by C. S. Marvel;[25] otherwise the above pro-

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[22] Chuit, *Helv. Chim. Acta*, **9**, 264 (1926); Chuit and Hauser *ibid.*. **12**, 850 (1929).

[23] Levene and Allen, *J. Biol. Chem.*, **27**, 443 (1916); cf. Adams and Marvel, *Univ. Illinois Bull.*, **20**, 50 (1922).

[24] Bouveault and Blanc, *Bull. soc. chim.*, [3] **31**, 666 (1904).

[25] Private communication.

cedure is similar to that which has also been used by Müller for preparing a series of glycols.[26]

Using the method described by Chuit,[22] we obtained from decamethylene glycol only a 70% yield of bromide and this was contaminated with bromohydrin. The following modification of this method gave a purer product and a better yield.

Dry hydrogen bromide was led into a well-stirred melt of 255 g. (1.47 moles) of decamethylene glycol in an open flask until the mass was saturated. The temperature of a metal-bath surrounding the flask was kept at 90–95°. After saturation was complete the bath temperature was raised to 135–140° and a slow stream of hydrogen bromide was led in for six hours. The reaction mass was then cooled, diluted with benzene and decanted from a small amount of water remaining in the flask. The benzene was then removed by distillation, and the product distilled under diminished pressure; yield, 376 g. (85.5%); b. p., 168–172° (10 mm.).

Anal. Calcd. for $C_{10}H_{20}Br_2$: Br, 53.33. Found: Br, 53.16, 53.16.

We are indebted to Mr. W. L. McEwen for the preparation of decamethylene glycol.

Summary

By the action of sodium on decamethylene bromide in ether a mixture of paraffins of the general formula $H—[(CH_2)_{10}]_x—H$ has been prepared. By fractional distillation in the molecular still and by crystallization, the following individuals have been isolated from this mixture: *n*-eicosane, *n*-triacontane, *n*-tetracontane, *n*-pentacontane, *n*-hexacontane, *n*-heptacontane. The last four of these are new, and the last one has a higher molecular weight than any pure paraffin hydrocarbon hitherto described. The residue remaining from the separation of the hydrocarbons named amounts to about 25% of the total and is composed of still higher members of the same series which it has not yet been possible to separate. The mechanism of the reaction and the properties of the products are discussed.

WILMINGTON, DELAWARE

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[26] Müller, *Monatsh.*, **49**, 27 (1928).