The Isomerization of Normal Heptane

BY GEORGE CALINGAERT AND HAROLD A. BEATTY

Nenitzescu and Dragan reported recently[1] that n-hexane and n-heptane heated on a water-bath in the presence of aluminum chloride yield a large amount of isohexane and isoheptane, respectively. The data presented do not substantiate these statements with great certainty: the starting materials were obviously not pure, the products obtained boiled over very wide ranges, and no further effort was made to identify the compounds present in the distillate.

The occurrence of such an isomerization is, perhaps, somewhat surprising, and appears incompatible with the findings of Schneider[2] that isohexane is more readily attacked by aluminum chloride than n-hexane. Nevertheless, preliminary work carried out in this Laboratory[3] confirmed the former reaction, in that a certain amount of 2-methylhexane was found in the products of the reaction of aluminum chloride on n-heptane. Since an isomerization of this kind may be of considerable interest, both theoretically and in petroleum technology, a more thorough investigation has now been carried out, the results of which are reported here. For this purpose, a technique was chosen which would remove the reaction products rapidly, in order to minimize secondary reactions, and an amount of product was prepared sufficiently large to permit a more complete fractionation and a more certain identification of the hydrocarbons present than has previously been attained.

In the prior work, a batch of n-heptane was refluxed for a long period of time with aluminum chloride. Under these conditions, the chloride rapidly becomes coated with a tarry material, and it is doubtful whether the prolonged heating is of any consequence. In the present work, the chloride was added in small portions to a batch of heptane which was kept boiling, while the lower-boiling products of the reaction (which include any isomeric heptanes) were continuously removed through a fractionating column. In this manner, the fresh chloride is brought each time in contact with n-heptane substantially free from the more volatile reaction products. The identification of the hydrocarbons formed was made more certain by subjecting the reaction product to rigorous fractionation, and by determination of the most distinctive physical properties of the different cuts so obtained.

The products boiling below 45° consisted principally of saturated material in the butane–pentane range. The residue boiling above 98° was a viscous, non-volatile tar of polymerization products, which was found to be essentially free from compounds in the octane–decane boiling range. Since the present investigation was primarily concerned with the identification of isomeric heptanes, the above products were measured only to obtain a complete material balance, but were not analyzed further. The remaining material, boiling between 45 and 98°, and shown by a bromine test to be completely saturated, was fractionated from three to five times through efficient fractionating columns. The refractive indices were determined all along the distillation curve, and the critical temperatures of solution in aniline (C. T. S.) were also determined for a number of selected cuts. Comparison of these data with the known physical properties of pure hydrocarbons[4] indicates the presence of several hexanes and heptanes and the absence of appreciable amounts of olefin, naphthene and aromatic hydrocarbons of similar boiling points. A quantitative estimation of the products obtained is given in Table I.

TABLE I

PRODUCTS OF REACTION OF ALUMINUM CHLORIDE ON n-HEPTANE

Basis: 100 parts of n-heptane reacted

Pentanes and below	64.6
2-Methylpentane	3.4
3-Methylpentane	2.0
n-Hexane	0.4
2,4-Dimethylpentane	1.5
2,2,3-Trimethylbutane	0.5
3,3-Dimethylpentane	0.4
2-Methylhexane	1.2
3-Methylhexane	1.6
Polymerization products	24.4

It is evident from the procedure used that the

(1) C. D. Nenitzescu and A. Dragan, Ber., 66B, 1892 (1933); see also A. D. Petrow, A. P. Meschtscherjakow and D. N. Andrejew, ibid., 68B, 1 (1935).

(2) H. G. R. Schneider, Thesis, Massachusetts Institute of Technology, Jan., 1928.

(3) G. Calingaert and D. T. Flood, THIS JOURNAL, 57, 956 (1935).

(4) G. Edgar and G. Calingaert, ibid., 51, 1540 (1929).

relative amounts of the different heptanes produced do not correspond to any straightforward isomerization of n-heptane which yields a mixture of isomers in thermodynamic equilibrium. Thus, while the 2,4- and 3,3-dimethyl isomers are formed in some quantity, there is apparently at most no more than a trace of the structurally similar 2,2- and 2,3-dimethylpentanes. On the other hand, the large amount of lower-boiling material and of polymerized products obtained suggests that the branched-chain heptanes may have resulted from the condensation of lower-boiling hydrocarbons formed in the reaction. However, the absence of appreciable amounts of octanes, nonanes and decanes renders this assumption doubtful. On the whole, it appears at the present time premature to speculate as to the reaction mechanism and the significance of the results.

Experimental

The reaction vessel was a 3-liter, 3-necked flask, heated in a water–glycerol bath, and fitted with a separatory funnel, a thermometer, a mechanical stirrer and a fractionating column. The latter was an adiabatic column, 1.8 cm. in diameter and 100 cm. long, with adjustable reflux and take-off, packed with 6–8 mm. crushed carborundum.

In a typical run, 500 g. of pure n-heptane (from Jeffrey pine, free from isomers[5]) was brought to boiling, and about 10 g. of aluminum chloride (Merck Reagent Grade, Sublimed) suspended in 10 g. of heptane was added every two minutes, with rapid stirring. A vigorous reaction took place, and a certain amount of gas and volatile material distilled off. The rate of addition of aluminum chloride, the reflux ratio in the column, and the heating bath were adjusted simultaneously to maintain a temperature of about 90° in the still-head and 96° in the reaction flask. The distillate was practically completely condensed by passing through two successive condensers at 15 and −80°. After weighing, these condensates were mixed and warmed up to room temperature, allowing the dissolved gases to escape. When a total of 1000 g. of aluminum chloride with an additional 1000 g. of n-heptane had been added, the accumulation of chloride in the flask made it necessary to stop the reaction, after which the heptane remaining was recovered by distillation. The addition of water to the residue in the flask yielded only a thick oil, and no volatile material. The weight of polymers formed was therefore estimated from the increase in weight of the reaction flask. The condensate was refractionated through the same column, ten fractions being collected, boiling up to 98°. This left a residue of about 55% which was practically pure n-heptane and was reused in subsequent runs.

In a total of seven runs, 9750 g. of n-heptane was thus treated with 6155 g. of aluminum chloride, giving the following products: material boiling below 45°, 2390 g.; material boiling from 45 to 98°, 960 g.; recovered n-heptane, 5450 g.; polymers, 950 g.

A test with bromine indicated that the material boiling from 45 to 98° was completely saturated. It was therefore refractionated without previous chemical treatment. The fractionation was carried out in an adiabatic, 10-mm. column of 140 cm. effective length, which was packed with 3.2 × 6.4 mm. double-cross wire forms,[6] and measured to have a very low hold-up and to be equivalent under total reflux to 25 theoretical plates. The reflux ratio used was approximately 50:1. The whole material was refractionated from one to three times, yielding finally (after slight corrections for handling losses and samples taken for refractive indices) 130 g. boiling below 45°, 450 g. boiling from 45 to 98.4° and estimated to contain 20 g. of n-heptane, and 380 g. of n-heptane.

The combined data on boiling points and refractive indices are given in Table II and Fig. 1. The C. T. S., Cottrell boiling points and refractive indices were deter-

TABLE II

FINAL FRACTIONATION OF REACTION PRODUCTS

B. p., (760 mm.), °C.	Total number fractionations employed	Total weight distilled, g.	n^{20}D
45.0	Three	0	1.3646
56.0	Three	10	1.3712
59.0	Three	16	1.3727
60.0	Three	42	1.3729
60.4	Three	89	
60.6	Four	119	
60.9	Four	140	
61.1	Five	151	1.3730
62.0	Five	171	1.3740
63.0	Five	185	1.3757
63.4	Five	199	1.3763
63.9	Five	204	1.3764
67.0	Five	214	1.3757
68.0	Five	218	1.3754
68.7	Five	221.5	1.3753
69.5	Five	224	1.3757
73.0	Four	228	1.3784
80.0	Four	233	1.3827
80.6	Four	243	1.3832
80.9	Four	283	1.3836
81.3	Four	298	1.3841
83.0	Five	308	1.3858
85.0	Five	312	1.3874
87.0	Five	316	1.3883
88.5	Five	318	1.3887
89.5	Five	323	1.3881
90.0	Five	332	1.3876
90.5	Five	358	1.3871
90.8	Five	380	1.3871
91.0	Five	396	1.3873
91.5	Five	410	1.3877
92.0	Four	419	1.3879
93.0	Four	425	1.3880
94.0	Four	428	1.3879
95.0	Four	431	
97.0	Four	438	
98.0	Four	444	
98.4	Four	450	1.3878

(5) Kremers, *J. Am. Pharm. Assocn.*, **9**, 857 (1920).

(6) M. R. Fenske, C. O. Tongberg and D. Quiggle, *Ind. Eng. Chem.*, **26**, 1169 (1934).

TABLE III

PHYSICAL PROPERTIES OF SELECTED FRACTIONS

Number	Boiling range (760 mm.), °C.	Cottrell b. p. (760 mm.), °C.	$n^{20}D$	C. T. S., °C.	$n^{20}D$	% Composition estimated from C. T. S.	
A	60.0–60.4	60.13	1.3780	73.6	69	79	2-methylpentane
					31	21	3-methylpentane
B	63.0–63.4		1.3760	70.3	82	83	3-methylpentane
					18	17	2-methylpentane
C	68.0–69.5		1.3753	69.2	·88	40	n-hexane
					12	60	3-methylpentane
D	80.6–80.9	80.68	1.3834	77.4	75	78	2,4-dimethylpentane
					25	22	2,2,3-trimethylbutane
E	88.5–89.5		1.3881	71.85	51	72,	3,3-dimethylpentane
					49	28	2-methylhexane
F	90.5–90.8	90.41	1.3871	72.0	57	58	3-methylhexane
					43	42	2-methylhexane
G	92.0–93.0		1.3879	71.1	78	83	3-methylhexane
					22	17	2-methylhexane

mined for some of the important fractions, and are given in Table III.

The data given in Tables II and III and Fig. 1 clearly indicate the presence of three hexanes, namely, 2-methylpentane, 3-methylpentane and n-hexane, and the absence of any naphthene and aromatic compounds in fractions A, B and C. The branched-chain heptane fractions cover a boiling range of only 12°, and contain at least five different hydrocarbons whose separation and identification is consequently more difficult. The large, narrow-boiling fraction D in Table III, judging from the refractive index and C. T. S. data, is most probably a mixture of 2,4-dimethylpentane and 2,2,3-trimethylbutane, which boil 0.1° apart; however, it could also consist of 2,4-dimethylpentane and a small amount (about 5%) of a naphthene hydrocarbon. Fraction E, corresponding to a peak in the index curve, can be a mixture of 2-methylhexane with either 2,3-dimethylpentane or 3,3-dimethylpentane; if so, the index curve shows that the high-index component is more volatile than 2-methylhexane, and must therefore be the 3,3-dimethyl isomer. On the other hand, this fraction may be 2-methylhexane together with 8–10% of 1,1-dimethylcyclopentane. Positive identification of the presence of such small amounts of naphthenes would have been difficult and was not attempted; however, the results in general suggest that none of these compounds was formed. Fractions F and G evidently contain 2-methylhexane and 3-methylhexane which, on account of the proximity of
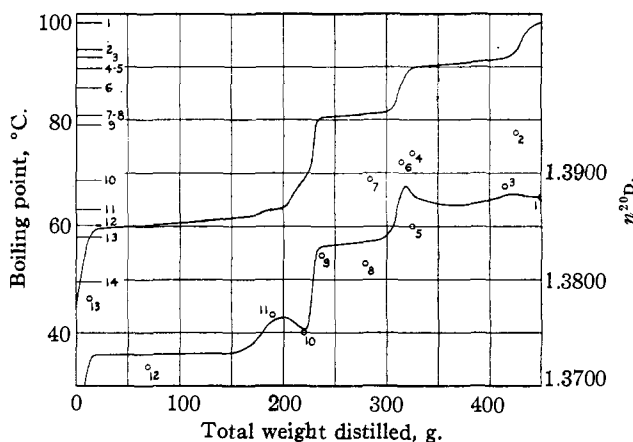

Fig. 1.—Boiling point (upper curve) and refractive index (lower curve) of the 45–98° material as a function of the total weight distilled. The boiling points and refractive indices of the pure hexanes and heptanes are indicated, respectively, by dashes on the boiling-point scale, and by circles located in the plot (on abscissae which intersect the boiling-point curve at the boiling points of the compounds), both numbered as follows:

1, n-heptane
2, 3-ethylpentane
3, 3-methylhexane
4, 2,3-dimethylpentane
5, 2-methylhexane
6, 3,3-dimethylpentane
7, 2,2,3-trimethylbutane
8, 2,4-dimethylpentane
9, 2,2-dimethylpentane
10, n-hexane
11, 3-methylpentane
12, 2-methylpentane
13, 2,3-dimethylbutane
14, 2,2-dimethylbutane

their boiling points, did not separate sharply.

Table III gives the calculated percentage compositions of the above fractions, based on the assumption that they are binary mixtures of paraffins, and that the indices of refraction and the C. T. S. are additive properties. Whenever the boiling range is narrow, the calculations by the two methods agree reasonably well, thus adding weight to the conclusions drawn above regarding the identity of the hydrocarbons present.

Summary

When pure *n*-heptane is refluxed with aluminum chloride, low-boiling fractions can be isolated for which the boiling points, refractive indices and C. T. S. in aniline indicate the presence of three hexanes, together with at least three, and probably five, of the eight branched-chain heptanes. The total amount of these hydrocarbons formed is about 6 and 5%, respectively, of the reacted *n*-heptane.


Studies in the Phenyl Ether Series. IV. Phenoxybenzene-4,4'-dithiol and Related Compounds

BY C. M. SUTER AND PAUL H. SCRUTCHFIELD

It was found some time ago[1] that the action of chlorosulfonic acid upon phenyl ether in the cold produced the 4,4'-disulfonyl chloride. It was believed to be of interest to prepare from this, through the intermediate dithiol and dithioglycolic acid, the polymeric thioindigo dye having the formula indicated.
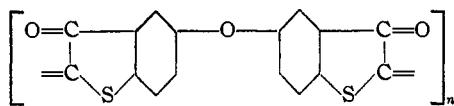
Although attempts to obtain this were not successful it seems desirable to report the preparation and properties of the intermediates.

Reduction of the disulfonyl chloride to the dithiol was found to be more difficult than had been anticipated, zinc and sulfuric acid or aluminum amalgam in alcohol and ether[2] yielding chiefly polymeric products. However, the use of stannous chloride and hydrogen chloride in glacial acetic acid, a method previously employed by Bogert and Bartlett[3] to reduce a nitronaphthalenesulfonyl chloride, gave good yields of the dithiol. At the same time a trace of hydrogen sulfide was formed as indicated by the stannic sulfide present in the reaction product.

The action of chlorosulfonic acid or fuming sulfuric acid of various concentrations upon the dithioglycolic acid either gave no ring closure or yielded water-soluble products evidently containing sulfonic acid groups. These latter were not investigated. Attempts to convert the acid chloride of the dithioglycolic acid into the cyclic compound by treatment with aluminum chloride were also unsuccessful. It seemed likely that ring

closure would be facilitated by the presence of a bromine para to the hydrogen through which this must occur but preliminary experiments upon the bromination of the dithioglycolic acid were not successful.

Experimental

Phenoxybenzene-4,4'-dithiol.—Hydrogen chloride was passed into a suspension of 80 g. (0.36 mole) of stannous chloride in 300 cc. of glacial acetic acid until the mixture became homogeneous. To this was added 11 g. (0.03 mole) of phenoxybenzene-4,4'-disulfonyl chloride and the mixture shaken for fifteen minutes. Reduction occurred readily with the evolution of heat. After filtering, the reaction mixture was poured into 300 cc. of concentrated hydrochloric acid to decompose the stannic salt of the dithiol. After recrystallizing from petroleum ether there was obtained 5 g. or 71% of the theoretical amount of product melting at 103–104°. The crude material was slightly yellow due to the stannic sulfide present. This was readily removed by boiling with concentrated hydrochloric acid, leaving a colorless product.

Although the purity of the dithiol was evident from its neutral equivalent, analyses for sulfur by the Parr bomb method gave slightly erratic results. These ranged from 26.39 to 27.36% with an average of 26.92% for seven determinations. Corresponding anomalies were not noted for the sulfides prepared from the dithiol.

Anal. Calcd. for $C_{12}H_{10}S_2O$: S, 27.34. Found: S, 26.92.

Phenoxybenzene-4,4'-dithioglycolic Acid.—Four and five-tenths grams (0.019 mole) of the dithiol and 7 g. (0.074 mole) of chloroacetic acid were dissolved in a slight excess of 5% potassium hydroxide and the solution allowed to stand overnight. The potassium salt which separated was dissolved in water and the solution acidified with hydrochloric acid. Crystallization from xylene gave 5.5 g. or 83% of the theoretical amount of the acid melting at 165–166°.

Anal. Calcd. for $C_{16}H_{14}S_2O_5$: S, 18.31; neut. eq., 175. Found: S, 18.37, 18.39; neut. eq., 174.

Various amounts of chlorosulfonic acid in acetic anhydride or in sulfuric acid either did not affect the dithio-

(1) Suter, THIS JOURNAL, **53**, 1112 (1931).
(2) Gebauer-Fuelnegg, *ibid.*, **49**, 1387 (1927).
(3) Bogert and Bartlett, *ibid.*, **53**, 4046 (1931).