and 1700 cc. of hydrogen collected (about 33% of the calcd.). Distillation at 1 mm. yields 11 g. of camphor anil.

Summary

A synthesis of camphor from bornyl chloride, passing through isobornylaniline and camphor anil, has been described. The yield of camphor from bornyl chloride by this procedure is 89%.

The action of nickel catalysts on isobornylaniline has been found to result, according to the conditions, in camphor anil, or a mixture of camphene and aniline.

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The Preparation of Some Mono- and Dialkylcyclohexanes

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As a part of an investigation carried on in this Laboratory of the detonation characteristics of individual hydrocarbons,[1] many of these compounds of various types were synthesized and it was thought desirable to publish the methods used for preparing certain series of the hydrocarbons in some quantity and of a reasonably high degree of purity, and also to give certain physical constants of these compounds, several of which will be described for the first time.

This first paper describes the preparation of mono- and dialkylcyclohexanes together with that of the corresponding intermediate cyclohexanols and cyclohexenes.

The general methods which have been used for the synthesis of alkylcyclohexanes are: (1) the reaction of zinc alkyls on bromocyclohexanes,[2] (2) the hydrogenation of alkylbenzenes,[3] and (3) the addition of Grignard reagents to cyclohexanones, yielding tertiary cyclohexanols which are converted to the corresponding paraffins either (a) by the reduction of their halides[4] or (b) by their dehydration and the hydrogenation of the resulting olefins.[5] A less general method is that of Bourguel,[6] who has prepared several monoalkylcyclohexanes by the hydrogenation of acetylene hydrocarbons.

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(1) Lovell, Campbell and Boyd, *Ind. Eng. Chem.*, **23**, 26 and 555 (1931), and a paper on the detonation characteristics of naphthene hydrocarbons now in preparation.

(2) Kursanoff, *Ber.*, **32**, 2972 (1899).

(3) Sabatier and Senderens, *Compt. rend.*, **132**, 566 (1901); and others.

(4) Zelinsky, *Ber.*, **34**, 2877 (1901); **35**, 2679 (1902); Knoevenagel, *Ann.*, **297**, 159 (1897); v. Auwers, *ibid.*, **420**, 96 (1919).

(5) Murat, *Ann. chim. phys.*, [8] **16**, 119 (1909); Sabatier and Mailhe, *ibid.*, [8] **10**, 551 (1907); Mailhe and Murat, *Bull. soc. chim.*, [4] **7**, 1083 (1910); Garland and Reid, THIS JOURNAL, **47**, 2337 (1925).

(6) Bourguel, *Bull. soc. chim.*, **41**, 1475 (1927).

Method 3b, which is superior to the others for the preparation of large quantities of hydrocarbons, is suitable for preparing the monoalkyl- and methylalkylcyclohexanes since cyclohexanone and the three methylcyclohexanones are readily obtained. This method, which has previously been used for the preparation of dicyclohexane and a few of the lower dialkylcyclohexanes, was employed in the preparation of most of the cyclohexanes described in this paper. This procedure offers in addition the corresponding alkylcyclohexenes, concerning which there is little information in the literature, and which were of interest in the detonation studies of naphthenes. The alcohol–olefin–paraffin method, of course, is limited by the availability of the cyclic ketones and also to those Grignard reagents which are known to give reasonably good yields of addition products.

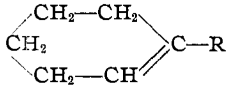
In agreement with other authors,[5] it was found that in most cases the addition of Grignard reagents to the cyclohexanones was accompanied by a side reaction in which the cyclohexanone was reduced to the corresponding cyclohexanol. Isopropyl- and isobutylmagnesium bromides exhibited this reducing action to the greatest extent. By keeping the reaction temperature below 5° less ketone was reduced.

Anhydrous aluminum sulfate[7] was used to dehydrate the monoalkylcyclohexanols and iodine[8] was used to dehydrate the dialkylcyclohexanols. Both catalysts gave good yields of olefins. A single distillation of the alcohols from iodine resulted in complete dehydration.

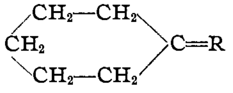
The alkylcyclohexenes were readily hydrogenated to the corresponding paraffins using platinum oxide as a catalyst according to the procedure for the hydrogenation of olefins as described by Adams and co-workers.[9]

All of the dialkylcyclohexanols and dialkylcyclohexanes admit of geometrical isomerism and are probably mixtures of the *cis* and *trans* forms. Evidence that this is true of the paraffins is the fact that the average boiling range of the dialkylcyclohexenes was 0.6° and that of the dialkylcyclohexanes was 1.9°.

There are two types of olefins (I and II) which might be formed by the dehydration of tertiary cyclohexanols, one in which the double bond lies in the ring and the other in which the double bond connects the side chain to the ring. Wallach[10] has dehydrated the lower tertiary mono- and dialkylcyclohexanols with dilute sulfuric acid and by oxidation of the olefins has shown them to have structure I. Several investigators have used



I



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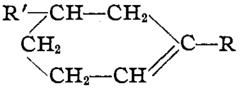

III

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(7) Chavanne and Becker, *Bull. soc. chim. Belg.*, **36**, 591 (1927).

(8) Hibbert, THIS JOURNAL, **37**, 1748 (1915).

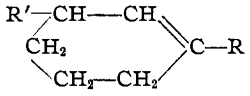
(9) Adams and Shriner, *ibid.*, **45**, 2171 (1923).

(10) Wallach, *Ann.*, **396**, 264 (1913).

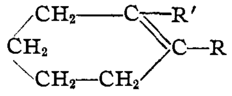
dehydrating agents other than sulfuric acid on these alcohols and found that the olefins obtained were the same as those described by Wallach as also were those prepared in the course of this investigation. Wallach has synthesized several olefins having structure II and found them to be different from the corresponding olefins prepared by the dehydration of tertiary cyclohexanols, and has also shown that olefins of structure II are readily rearranged to those of structure I. In view of these facts, it is assumed that all of the olefins described in this paper have structure I. This consequently assigns a definite structure to the olefins prepared from the 1-alkyl- and 1,4-dialkylcyclohexanols.

The dehydration of 1,3-dialkylcyclohexanols might give rise to two olefins (III and IV) in both of which the double bond lies in the ring. Wallach dehydrated 1,3-dimethylcyclohexanol with sulfuric acid and found that the product was the olefin of structure III. This alcohol when dehydrated with iodine yielded the same olefin as that obtained by Wallach. The boiling ranges of the olefins prepared from the higher 1,3-dialkylcyclohexanols indicate that each is one compound and it is assumed that they too have structure III.

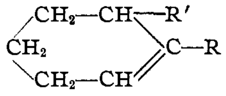
Two olefins (V and VI) might likewise be formed by the dehydration of 1,2-dialkylcyclohexanols. Wallach has further shown that the olefin obtained by dehydrating 1,2-dimethylcyclohexanol with sulfuric acid is that one having structure V. Dehydration of this alcohol with iodine yielded the same olefin as that obtained by Wallach. As before it is assumed that the higher 1,2-dialkylcyclohexanols behave similarly and that the olefins produced by their dehydration with iodine have structure V.



IV



V



VI

The starting materials for this work were cyclohexanone, which is readily obtained pure, and the three methylcyclohexanols which were prepared by the Deutsche Hydrierwerke. That these latter were free from isomers is evidenced by the melting points of their phenyl urethan derivatives and the constants of the three ketones prepared from the alcohols by oxidation (Tables I and II). All of the by-products which arise during the reactions are readily removed by chemical means with the exception of the secondary cyclohexanols which are formed by the reduction of the cyclohexanones during the addition of the Grignard reagent. These were separated from the tertiary cyclohexanols by fractionation at reduced pressure.

All but seventeen of the compounds prepared during this investigation and described in the following tables have been reported by other authors, although, with the exception of the monoalkyl- and dimethylcyclohexanes and a few of the lower olefins, no especial attempt had been made to obtain the hydrocarbons in a highly pure form. The cyclohexanes prepared by the hydrogenation of the corresponding aromatic compounds, as indicated in Table V, have been prepared by this method and described by a number of other investigators; however, since they complete certain isomeric groups, it seemed desirable to include them here.

Experimental Part

Preparation of Methylcyclohexanones.—These ketones were prepared by chromic acid oxidation of the corresponding cyclohexanols.

Seven moles of methylcyclohexanol was mixed with a solution of 1.4 moles of sodium dichromate in 1750 cc. of water and heated to 80°. While this mixture was being stirred, a solution of 1.4 moles of sodium dichromate and 11 moles of sulfuric acid in 1750 cc. of water was added dropwise at such a rate as to keep the temperature at about 80°. The time required for completing the reaction was about twelve hours. The ketone was distilled from the reaction mixture, separated from the water layer, and distilled through a 51-cm. spiral fractionating column. The properties and yields of the three ketones are listed in Table II.

TABLE I

PROPERTIES OF THE METHYLCYCLOHEXANOLS

Methylcyclohexanol	2-	3-	4-
d^{20}_{20}	0.930	0.920	0.920
M. p. of phenyl urethan, °C.	104.5	92	123

TABLE II

PROPERTIES AND YIELDS OF THE METHYLCYCLOHEXANONES

Methylcyclohexanone	B. p., °C. (corr.)	d^{20}_{20}	n^{20}_{D}	M. p. of semicarbazone, °C.	Yield, %
2-	164.8–165.0	0.926	1.4487	191	85
3-	168.6–168.9	.914	1.4463	182	78
4-	171.4–171.5	.917	1.4462	196	70

Preparation of Tertiary Cyclohexanols.—The Grignard reagent, 7 moles in 2.5 liters of ether, was prepared in the usual manner. Six moles of the cyclohexanone, in an equal volume of ether, was added slowly to the cooled Grignard reagent. During this addition, the temperature of the reaction mixture was kept below 5° and the mixture was stirred continuously. The time required for the addition of the ketone was about eight hours. When all of the ketone had been added, the reaction mixture was allowed to warm to room temperature and was then hydrolyzed with ice and hydrochloric acid. The ether solution of the cyclohexanol was washed with a saturated solution of sodium bisulfite to remove any unchanged ketone, washed several times with water, and dried over anhydrous sodium carbonate. The ether was removed by distillation and the alcohol fractionated under reduced pressure. The data on these alcohols are given in Table III.

Preparation of Alkylcyclohexenes.—The monoalkylcyclohexanols were dehydrated by distillation from anhydrous aluminum sulfate. Fifty grams of anhydrous aluminum sulfate was placed in a 1-liter Claissen flask which was fitted with a dropping funnel and a condenser set up for distillation. A small amount of the alcohol was added and the flask heated by means of an alloy bath until the olefin and water distilled slowly and evenly, the dehydration beginning at about 150°. The remainder of the alcohol (approx. 250 g.) was then slowly added as the distillation continued. With some of the

TABLE III

PROPERTIES AND YIELDS OF THE ALKYLCYCLOHEXANOLS

Cyclohexanol (* New compounds)	B. p., °C.	Press., mm. Hg	d_{20}^{20}	n_D^{20}	Yield, %	Analyses, % Calcd. C	H	Found C	H
1-Methyl-	53–54	7	0.932	1.4610	64				
1-Ethyl-	61–63	7	.934	1.4633	62				
1-*n*-Propyl-	84–87	15	.930	1.4635	57				
1-Isopropyl-	66–69	7	.942	1.4648	41				
*1-*n*-Butyl-	88–91	7	.916	1.4648	48	76.85	12.91	76.32	12.75
*1-*n*-Amyl-	96–96.5	5	.916	1.4668	54	77.56	13.03	77.15	12.97
1-Isoamyl-	96–97	7	.907	1.4646	58				
1-Cyclohexyl-	114–115	7	M. p. 51°		53				
1-Phenyl-	112–113	5	M. p. 60°		60				
1,2-Dimethyl-	119–121	164	.921	1.4620	67				
1-Ethyl-2-methyl-	55–57	2	.924	1.4670	92				
1-*n*-Propyl-2-methyl-	65–67	2	.913	1.4653	57				
*1-*n*-Butyl-2-methyl-	76–80	2	.908	1.4665	65	77.56	13.03	77.03	12.99
*1-*n*-Amyl-2-methyl-	89–90	1.5	.902	1.4664	63	78.18	13.13	77.85	13.12
1,3-Dimethyl-[a]					80[b]				
1-Ethyl-3-methyl-	62–63.5	3	.909	1.4611	93				
1-*n*-Propyl-3-methyl-	72–74	3	.901	1.4592	72				
*1-*n*-Butyl-3-methyl-	85–86	2	.896	1.4625	70	77.56	13.03	77.36	13.05
1-Isobutyl-3-methyl-[c]					6[b]				
1-Ethyl-4-methyl-	50–52	2	.910	1.4614	69				
1-*n*-Propyl-4-methyl-	65–67	1	.900	1.4600	52				
*1-*n*-Butyl-4-methyl-	74–76	2	.897	1.4621	44	77.56	13.03	76.96	12.93

[a] This alcohol dehydrated on vacuum distillation due, probably, to the presence of a small amount of iodine. [b] Calculated from the amount of olefin produced. [c] So large an amount of 3-methylcyclohexanol was present with this alcohol that it was not isolated but dehydrated directly.

lower boiling alcohols it was necessary to repeat the procedure in order to obtain complete dehydration. 1-Phenylcyclohexanol and 1-cyclohexylcyclohexanol were dehydrated by distillation from aluminum sulfate under reduced pressure. The olefins were dried over calcium chloride, refluxed with sodium and distilled through a 51-cm. spiral fractionating column.

The dialkylcyclohexanols were dehydrated by heating about 750 g. of the alcohol containing 2 g. of iodine. At about 100° dehydration began and the temperature was adjusted so that the olefin and water distilled slowly. Complete dehydration of the alcohol was obtained by one distillation. The olefin was washed with a sodium thiosulfate solution to remove any free iodine and dried over calcium chloride. It was then refluxed with sodium to remove any combined iodine or secondary cyclohexanol that might have been present and then distilled through the fractionating column.

As intimated previously, the product of the reaction between isobutylmagnesium bromide and 3-methylcyclohexanone was a mixture of 1-isobutyl-3-methylcyclohexanol (10%) and 3-methylcyclohexanol (90%). Distillation of this mixture from iodine yielded a mixture of 2-isobutyl-4-methylcyclohexene and the unchanged 3-methylcyclohexanol. Repeated fractionation of this product gave 3-methylcyclohexanol and an azeotropic mixture of 3-methylcyclohexanol (60%) and 2-isobutyl-4-methylcyclohexene (40%). The boiling point of this mixture was 167–168° (uncorr.) and its specific gravity was d_{20}^{20} 0.880. It was resolved by washing five times with 50% aqueous ethyl alcohol, followed by washing with water. The olefin was dried over calcium chloride, refluxed with sodium and distilled. The data on the olefins are given in Table IV.

Preparation of Alkylcyclohexanes.—Hydrogenation of the cyclohexenes was carried out in 2-mole runs. The olefin, in 100 cc. of glacial acetic acid, was readily hydro-

TABLE IV

PROPERTIES OF THE ALKYLCYCLOHEXENES[a]

Cyclohexene (* New compounds)	B. p., °C. (corr.)	d_{20}^{20}	n_D^{20}	Analyses, % Calcd. C	Analyses, % Calcd. H	Analyses, % Found C	Analyses, % Found H
1-Methyl-	109.0–110.0	0.809	1.4498				
1-Ethyl-	135.7–136.6	.828	1.4583				
1-*n*-Propyl-	154.7–157.7	.826	1.4578				
1-Isopropyl-	151.7–154.5	830	1.4594				
*1-*n*-Butyl-	180.8–182.9	828	1.4591	86.86	13.14	86.47	13.14
*1-*n*-Amyl-	203.4–205.0	.831	1.4605	86.75	13.25	86.33	13.20
1-Isoamyl-	194.5–196.5	.826	1.4596				
1-Cyclohexyl-	88–89 (4 mm.)	.906	1.4916				
1-Phenyl-	101-102 (4 mm.)	.986	1.5700				
1,2-Dimethyl-	135.4–135.9	.826	1.4590				
1-Ethyl-2-methyl-	156.7–157.0	.832	1.4630				
1-*n*-Propyl-2-methyl-	177.3–177.8	.832	1.4627				
*1-*n*-Butyl-2-methyl-	197.8–199.1	.833	1.4637	86.75	13.25	86.04	13.33
*1-*n*-Amyl-2-methyl-	218.9–219.7	.834	1.4646	86.65	13.35	86.21	13.41
2,4-Dimethyl-	127.4–127.8	.805	1.4480				
2-Ethyl-4-methyl-	151.9–152.1	.815	1.4544				
2-*n*-Propyl-4-methyl-	172.6–173.2	.816	1.4546				
*2-*n*-Butyl-4-methyl-	195.2–195.7	.820	1.4574	86.75	13.25	86.63	13.15
2-Isobutyl-4-methyl-	184.1–186.2	.812	1.4530				
1-Ethyl-4-methyl-	151.5–151.7	.814	1.4528				
1-*n*-Propyl-4-methyl-	173.2–174.2	.815	1.4533				
*1-*n*-Butyl-4-methyl-	196.3–197.1	.818	1.4558	86.75	13.25	86.33	13.15

[a] These olefins were obtained in approximately 80% yields, the losses being the usual ones due to manipulation.

genated by shaking with hydrogen under an initial pressure of 45 lb./sq. in., using 0.5 g. of platinum oxide as the catalyst. After filtering the solution from the catalyst, the hydrocarbon was separated from the acetic acid by the addition of water. It was washed free from any unchanged olefin with concentrated sulfuric acid, dried over calcium chloride, refluxed with sodium and distilled through the column.

The alkylbenzenes, which were hydrogenated to cyclohexanes (Table V), were treated with dilute alkaline potassium permanganate solution and refluxed with sodium to remove any substances which might poison the catalyst. One-half mole of the aromatic hydrocarbon in glacial acetic acid was hydrogenated using platinum oxide as the catalyst. Frequent reactivation of the catalyst, by shaking the mixture in air, and several additions of fresh catalyst were necessary before the hydrogenation was completed. When no more hydrogen was absorbed, the mixture was treated as described above with the exception that any unchanged aromatic hydrocarbon was removed by washing with a cooled mixture of concentrated nitric and sulfuric acids (1:2 by volume). Table V lists the data on the alkylcyclohexanes.

TABLE V

PROPERTIES OF THE ALKYLCYCLOHEXANES[a]

Cyclohexane (* New compounds)	B. p., °C. (corr.)	d_{20}^{20}	n_D^{20}	Method of prep.[b]	Analyses, % Calcd. C	Analyses, % Calcd. H	Analyses, % Found C	Analyses, % Found H
Methyl-	99.8-100.8	0.769	1.4230	1				
Ethyl-	130.1-130.7	.787	1.4332	1				
n-Propyl-	154.9-155.0	.793	1.4370	1				

TABLE V (*Concluded*)

Cyclohexane (* New compounds)	B. p., °C. (corr.)	d_{20}^{20}	n_D^{20}	Method of prep.[b]	Analyses, % Calcd. C	H	Found C	H
Isopropyl-	151.7–153.0	0.799	1.4411	1				
n-Butyl-	180.1–181.2	.799	1.4408	1				
Isobutyl-	170.8–171.7	.797	1.4391	2				
Sec-butyl-	178.5–179.5	.811	1.4458	2				
Tert-butyl-	169.9–171.4	.813	1.4464	2				
n-Amyl-	201.4–201.9	.804	1.4428	1				
Isoamyl-	193.8–195.2	.800	1.4420	1				
Tert-amyl-	193.3–195.2	.821	1.4510	2				
Cyclohexyl-	236.5–237.5	.877	1.4798	1				
1,2-Dimethyl-	126.4–128.9	.792	1.4332	1				
1,2-Methylethyl-	152.6–154.7	.805	1.4400	1				
1,2-Methyl-*n*-propyl-	175.2–177.0	.810	1.4445	1				
*1,2-Methyl-*n*-butyl-	195.6–198.1	.813	1.4467	1	85.61	14.39	85.02	14.45
*1,2-Methyl-*n*-amyl-	215.8–219.1	.816	1.4487	1	85.61	14.39	85.45	14.35
1,3-Dimethyl-	120.9–122.5	.774	1.4253	1				
1,3-Methylethyl-	148.4–150.0	.791	1.4344	1				
1,3-Methyl-*n*-propyl-	171.1–173.0	.796	1.4377	1				
*1,3-Methyl-*n*-butyl-	194.8–195.2	.801	1.4418	1	85.61	14.39	85.37	14.32
1,4-Dimethyl-	122.0–124.0	.777	1.4271	2				
1,4-Methylethyl-	150.1–151.0	.791	1.4343	1				
*1,4-Methyl-*n*-propyl-	174.3–177.1	.798	1.4393	1	85.61	14.39	85.06	14.42
*1,4-Methyl-*n*-butyl-	195.9–196.6	.807	1.4441	1	85.61	14.39	85.27	14.38
1,3-Diethyl-	173.5–174.5	.800	1.4409	2				
1,4-Diethyl-	174.6–176.4	.802	1.4415	2				
1,3,5-Trimethyl-	139.3–141.4	.777	1.4316	2				

[a] These paraffins were obtained in approximately 80% yields, the losses being the usual ones due to manipulation. [b] (1) Alcohol–olefin–paraffin method. (2) Hydrogenation of the corresponding alkylbenzene.

Summary

The preparation and physical constants of several mono- and dialkylcyclohexanes prepared by the alcohol–olefin–paraffin method have been described. Also a description has been given of a few alkylcyclohexanes, prepared by the hydrogenation of the corresponding aromatic hydrocarbons.

Of the seventy-two cyclic compounds presented in this paper, seventeen have been described for the first time.

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