2. By means of this apparatus the last 10–15% of the ethyl esters of the fatty acids of chaulmoogra oil were distilled without any appreciable decomposition. From the distillation products the following new substances were isolated: (*a*) taraktogenic acid, $C_{36}H_{60}O_6$; m. p., 113.5° (uncorr.); iodine no., 42.51; (*b*) isogadoleic acid, $C_{20}H_{38}O_2$; m. p., 65.5–66° (uncorr.); (*c*) a lactone-like substance, $C_{18}H_{32}O_2$; m. p., -11.6 (uncorr.); (*d*) an acid, new in the oil, possibly arachidic acid; (*e*) a brown, resinous material which is insoluble in organic solvents; (*f*) two unidentified solids, probably acids.

3. The presence of chaulmoogric and hydnocarpic acids, and these only, in the lighter fractions of the esters of the non-volatile acids is confirmed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

SOME NEW DERIVATIVES OF CYCLOHEXANONE[1]

BY CLARENCE E. GARLAND[2] AND E. EMMET REID

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Introduction

The present investigation had a double object: to obtain more information about the condensation products of cyclohexanone and to prepare alkyl substitution products of cyclohexane. These hydrocarbons belong to the class of naphthenes that occur in petroleum in large amounts and great variety, but about which little is known. Every member of this class that is prepared adds that much to the foundation which is needed for a study of the naphthenes.

Historical

Vorländer and Hobohm[3] condensed benzaldehyde with cyclohexanone in alcoholic solution, using sodium hydroxide as a condensing agent. Later, Wallach[4] prepared a series of condensation products of cyclohexanone using a number of aldehydes. All of these gave yellow derivatives except the salicylaldehyde, which was considered to have formed an anhydride between the two hydroxyls.

Borsche, using the method of Paal,[5] hydrogenated a series of unsaturated ketones.

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[1] This paper was presented before the Organic Division at the 67th Meeting of the American Chemical Society, Washington, D. C., April 23, 1924.

[2] From the Doctor's dissertation of Clarence E. Garland, Johns Hopkins University, 1924.

[3] Vorländer and Hobohm, *Ber.*, **29**, 1840 (1896).

[4] Wallach, *Ber.*, **40**, 71 (1907); *Göttingen Nachrichten*, **404** (1907); "Terpene und Campher," **1914**, p. 405.

[5] Borsche, *Ber.*, **45**, 46 (1912).

On treating pulegone and menthone with methylmagnesium iodide, Grignard[6] obtained tertiary alcohols, but these were partly dehydrated to give the unsaturated hydrocarbons. He made no further attempt to prepare alcohols from these ketones but completed the dehydration of his product at 100° with acetic anhydride. He considered that the elimination of water took place between the hydroxyl and the hydrogen of the methyl group to give methylene derivatives of *p*-menthene and *p*-menthane, respectively.

From cyclohexanone a series of tertiary alcohols was prepared by Sabatier and Mailhe[7] by means of the Grignard reaction. They found little or no dehydration during the reaction, but state that in some cases the yields were rather low. This may have been due to dehydration with subsequent polymerization. From these alcohols they produced the corresponding ethylene hydrocarbons by dehydration with fused zinc chloride at 160°.

Kohler[8] has made a study of the reaction of Grignard reagents on α,β unsaturated ketones. These behave generally like the corresponding open-chain compounds, except that in some cases1, 4- addition takes place to form saturated ketones.

There has been some question as to whether the condensation product of cyclohexanone with itself is cyclohexylidene-cyclohexanone or cyclohexenyl-cyclohexanone. At first, Wallach[9] favored the latter structure, but Braun and Ritter[10] have shown that the former, in which the double bond is between the two rings, is the correct one.

When a tertiary alcohol formed from a cyclohexanone by the Grignard reaction is dehydrated, Wallach[11] has shown that the resulting double bond is in the ring, so that the product is an alkyl cyclohexene.

Results

Two molecules each of *p*-toluic aldehyde, 2,4-dimethyl- and *p*-bromobenzaldehyde have been condensed with cyclohexanone, and one of furfural with cyclohexylidene-cyclohexanone.

The general properties of the unsaturated 2,6 substituted cyclohexanones thus prepared are very similar to those of the compounds produced by condensation of aromatic aldehydes with the simpler aliphatic ketones. They are relatively less soluble in cold organic solvents and for the most part melt at higher temperatures and crystallize better. Their yellowish-orange color is attributed to the chromophoric effect of the double bonds in alternate position to the carbonyl group. They possess the property of halochromism which is frequently observed in unsaturated substances

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[6] Grignard, *Ann. chim. phys.*, [7] **24,** 483 (1901).

[7] Sabatier and Mailhe, *Compt. rend.*, **138,** 1321 (1904).

[8] Kohler, *Am. Chem. J.*, **37,** 269 (1907).

[9] Wallach, *Ann.*, **381,** 95 (1911); *Ber.*, **40,** 70 (1907).

[10] Braun and Ritter, *Ber.*, **55B,** 3798 (1922).

[11] Wallach, *Ann.*, **396,** 264 (1913).

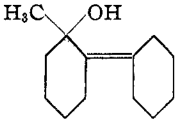
having carbonyl groups. They form highly colored salts with acids. The ethylenic bonds in these ketones have the usual reactivity toward halogens, especially bromine, and are possibly more reactive in this respect because of the carbonyl. By this condensation, a mono- or disubstitution product is formed, but it is very difficult to prepare the mono derivative alone since the reaction rate of the second substitution is apparently greater than that of the first.

Attempts were made to condense propionic and butyric aldehydes and heptaldehyde with cyclohexanone. A vigorous reaction took place in each case, but the aldehyde condensed with itself leaving the ketone untouched.

The 2,6-dibenzyl-, dianisyl-, dipiperonyl-, di-*p*-tolylyl, di(2,4-dimethyl)-benzyl- and di-*p*-chlorobenzyl-cyclohexanones have been obtained by hydrogenating, with platinum oxide as catalyst, the corresponding unsaturated ketones. On saturation, the chromophoric grouping disappears and white, crystalline derivatives are obtained which are more soluble in alcohol and glacial acetic acid than the unsaturated compounds. These do not give colored derivatives with acids as do the unsaturated ketones.

Neither the saturated nor the unsaturated substituted ketones react with the semicarbazide. This inactivity may be attributed to the presence of large groups on both sides of the carbonyl. (Compare the work of Haller[12] on substitutions in the α,α' positions and the effect on reactivity of the carbonyl group.)

Tertiary alcohols I and II have been made by treating cyclohexylidene-cyclohexanone with methyl and ethyl Grignard reagents. These alcohols have been hydrogenated. Both the unsaturated and the saturated alcohols III and IV were dehydrated to the corresponding hydrocarbons 1-methyl-6-cyclohexylidene-Δ'-cyclohexene, V; 1-ethyl-6-cyclohexylidene-Δ'-cyclohexene, VI; and 1-ethyl-2-cyclohexyl-cyclohexene, VII. These were hydrogenated to 1-methyl-2-cyclohexyl-cyclohexane and 1-ethyl-2-cyclohexyl-cyclohexane, VIII and IX.



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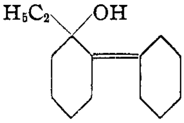

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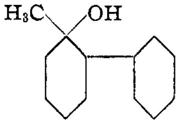

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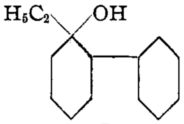

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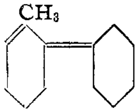

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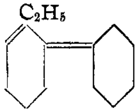

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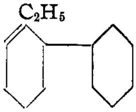
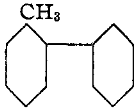


VII



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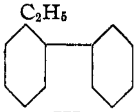

IX

Experimental Part

Materials.—Commercial cyclohexanol from Germany was used. It contained 14% of the ketone. An attempt was made to dehydrogenate it by passing it over copper

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[12] Haller, *Bull. soc. chim.*, **31**, 1076 (1922).

turnings at 280°,[13] but only 36% of the desired ketone was obtained, the rest seeming to go to tetrahydrobenzene, cyclohexane and benzene. Oxidation by chromate mixture gave 65%, provided the temperature was kept low. A cold mixture of 300 g. of sodium dichromate, 80 g. of sulfuric acid and 400 cc. of water was added slowly to 300 g. of cyclohexanol well cooled with ice. The oil was separated and steam distilled. The oil thus obtained was shaken with a concentrated solution of sodium bisulfite, the mixture being finally heated to dissolve the addition product and the remaining oil separated. The ketone was set free by sodium carbonate and steam distilled. It was allowed to stand over calcium chloride to free it from traces of the alcohol and water, and then distilled at 156.1–156.8°.

In preparing cyclohexylidene-cyclohexanone, pure cyclohexanone was treated with dry hydrogen chloride according to the method mentioned but not described in detail by Wallach. The flask containing the ketone was well cooled in ice. A crystalline addition product formed which melted at 41–43° and evolved hydrogen chloride when heated. This addition compound was decomposed with sodium carbonate solution and the oily layer washed and dried over calcium chloride. It was then warmed with dry sodium carbonate to remove the last trace of acid before fractionation in a vacuum. The dicyclic ketone boils at 273–275° (760 mm.); 150–152° (20 mm.); d_{18}, 1.005; *n*, 1.5082; the semicarbazone melts at 179–181°; the oxime melts at 146–150°.

Condensation of Aldehydes with Cyclohexanone and with Cyclohexylidene-cyclohexanone. Hydrogenation of the Saturated Ketones.—The method of preparing these condensation products was to treat 1 part of ketone and 2 equivalents of aldehyde in 5 parts of alcohol with 2 parts of a 10% solution of sodium hydroxide as a condensing agent. On standing, the 2,6 disubstituted unsaturated ketone separated in the form of yellow crystals. Glacial acetic acid was used for recrystallization. All of these compounds are very slightly soluble in ether or alcohol. The yields were 60–70%.

TABLE I

2,6 DISUBSTITUTED CYCLOHEXANONES, RCH:C_6H_6O:CHR. UNSATURATED

Substance	Cryst. Form	M. p., °C.	% Calcd. C	% Calcd. H	% Found C	% Found H
	Unsaturated—all yellow					
Di-*p*-tolylyl	needles	170.1	87.32	7.35	87.28	7.07
Di-(2,4-dimethylbenzal)	prisms	115.5	87.28	7.90	87.60	7.88
2-Furfural-6-cyclohexylidene	plates	80	79.69	7.82	79.41	7.87
Di-*p*-bromobenzal	plates	155.7	Br Calcd.: 37.01		Found: 36.96	

2,6-Dibenzal-cyclohexanone tetrabromide was obtained by adding bromine to a chloroform solution of the unsaturated ketone. White, prismatic crystals were obtained on recrystallization from alcohol; m. p., 184°, with decomposition (evolution of hydrogen bromide).

Anal. Calcd. for $C_{20}H_{18}OBr_4$: Br, 53.83. Found: 53.95.

Saturated Ketones, $RCH_2.C_6H_8O.CH_2R$.—These were prepared by hydrogenating the corresponding unsaturated compounds by shaking at room temperature with hydrogen under a pressure of 1 to 2 atmospheres using the platinum oxide catalyst. This was obtained by the method of Adams and Voorhees[14] with one slight modification. On filtering off the platinum oxide considerable of the material remains in colloidal solution. This was boiled for a few minutes with sodium carbonate, which precipitates

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[13] Holleman, *Rec. trav. chim.*, **24,** 19 (1905). Sabatier and Senderens, *Compt. rend.*, **137,** 1025 (1903).

[14] Adams and Voorhees, THIS JOURNAL, **44,** 1397 (1922).

practically all of the oxide. This was found to have catalytic properties apparently equal to those of the substance from the first filtration.

The unsaturated ketones were suspended with 1 g. of the catalyst in 250 cc. of 95% alcohol in which they are only slightly soluble. Shaking was continued until hydrogenation was complete. This was evident by the disappearance of the yellow color of the unsaturated ketone, though the products were tested for bromine absorption to make sure. In all cases it was found necessary to aerate the catalyst at intervals to renew its activity. The amount of hydrogen absorbed was estimated from the differences in the manometer readings. The apparatus and method were checked by hydrogenating tetrahydrobenzene. The volumes given are reduced to standard conditions. High accuracy in the volume measurements was not considered necessary and the values given are to be regarded as approximate only. Solution commonly took place simultaneously with hydrogenation, as the saturated ketones are usually much more soluble in alcohol than the unsaturated. The catalyst was filtered off and the alcohol evaporated until the product crystallized.

The amounts of ketones taken and the volumes of hydrogen absorbed are given in Table II.

Table II

2,6 Disubstituted Cyclohexanones, $RCH_2.C_6H_8O.CH_2R$. Saturated

Substance	G.	Vol. calcd. Cc.	Hydrogen, cc. absorbed	Form	M. p., °C.
Dibenzyl	20	3270	3250	plates	121
Di-*p*-methylbenzyl	8	1180	1160	plates	111.8
Di-2,4-dimethylbenzyl	1.55	206	200	needles	105
Di-*p*-chlorobenzyl	5	625	625	needles	143
Dianisyl	4	530	530	plates	157
Dipiperonyl	20	2540	2505	needles	146

Anal. Calcd. for di-*p*-methylbenzyl: C, 86.20; H, 8.56. Found: C, 86.28; H, 8.54.

Calcd. for di-2,4-dimethylbenzyl: C, 86.19; H, 9.03. Found: C, 86.41; H, 9.14.

Calcd. for di-*p*-chlorobenzyl: Cl, 20.43. Found: 20.19.

Calcd. for dianisyl: C, 78.12; H, 7.73. Found: C, 78.44; H, 7.63.

Calcd. for dipiperonyl: C, 72.10; H, 6.05. Found: C, 72.26; H, 5.92.

A preparation of 2,6-dibenzyl-cyclohexanone is described by Borsche, who used palladium and hydrogen. The melting point was given as 114°. Our product crystallized in white plates that melted sharply at 121°. A material having the same melting point was also prepared by hydrogenation with 2% sodium amalgam and alcohol.

Tertiary Alcohols from Cyclohexylidene-cyclohexanone.—It has proved to be impossible to effect complete reaction of the Grignard reagent with this ketone, without more or less dehydration of the tertiary alcohol formed. When a 10% excess of the Grignard reagent was used and the mixture heated for one hour to complete the reaction, the product contained unreacted ketone and also 7% of the hydrocarbon resulting from dehydration. When the ketone was added to 2 equivalents of the Grignard reagent and the mixture allowed to stand overnight, all of the ketone was used up, but 40% of the hydrocarbon was found.

The method developed which gave satisfactory results consisted in adding the Grignard reagent slowly to an excess of the ketone and then allowing the reaction mixture to stand for three days before decomposition to give the tertiary alcohols. A considerable part of the ketone was found to be unacted upon, but this was removed by semicarbazide. After the Grignard complex had been decomposed in the usual way and the ether distilled, the oil was diluted with 10 volumes of alcohol. Semicarbazide hydrochloride, dissolved in a little water and alcohol, and the equivalent quantity of potassium acetate were added to the alcohol solution. After several days the semicarbazone precipitated. This process was repeated until no more precipitate separated. After the alcohol had been distilled from the filtrate the tertiary alcohol was obtained by steam distillation. In all cases mixed melting points of the semicarbazones formed during purification with samples prepared from the pure ketone indicated that no new ketone was being formed by addition to the double bond. The ethyl derivative was more easily prepared in a state of purity than the methyl. Apparently the ethyl Grignard reagent had less dehydrating tendency or the alcohol formed was less easily dehydrated than in the case of the methyl compound.

Preparation of the acetates of these tertiary alcohols was attempted, but apparently they were more easily dehydrated than esterified and only so small amounts of the acetates resulted that they could not be purified.

Likewise, treatment with diphenyl-carbamide chloride in the presence of pyridine resulted in dehydration instead of a diphenylurethan.

The saturated alcohols III and IV were prepared by hydrogenating I and II, the corresponding unsaturated alcohols. The same conditions were used as for the ketones except that the alcohols were entirely in solution all of the time on account of their greater solubility in 95% alcohol. After the catalyst had been filtered off, the excess of solvent was distilled, the product purified by steam distillation and fractionated under reduced

TABLE III

TERTIARY ALCOHOLS, 1-METHYL OR ETHYL-2-CYCLOHEXYLIDENE OR CYCLOHEXYL-CYCLOHEXANOL (I)

No.	Substituents	B. p. (20 mm.), °C.	d_4^0	d_4^{20}
I	1-Methyl-2-cyclohexylidene	146–148	0.9972	0.9841
II	1-Ethyl-2-cyclohexylidene	155–157	.9993	.9863
III	1-Methyl-2-cyclohexyl	148.5–150	.9850	.9719
IV	1-Ethyl-2-cyclohexyl	154–156	.9927	.9778

REFRACTIONS, MOLECULAR REFRACTIONS AND ANALYSES

No.	*n*	*M* Calcd.	*M* Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
I	1.5107	58.89	58.57	80.33	80.80	11.43	11.25
II	1.5120	63.51	62.85	80.68	80.61	11.63	11.50
III	1.5019	59.36	59.23	79.56	79.93	12.31	11.89
IV	1.5058	63.98	63.21	79.94	80.10	12.47	11.80

pressure. For 40 g. of Compound I the hydrogen absorbed was 4595 cc. compared with 4615 cc. calculated, while 40 g. of Compound II took 4275 instead of 4300 cc.

Hydrocarbons by Dehydration and by Hydrogenation of Unsaturated and Saturated Tertiary Alcohols.—Dehydration of the tertiary alcohols I, II and IV, was brought about by heating with phthalic anhydride for five to six hours at 165–170°. This temperature was found to be necessary for complete dehydration. The hydrocarbons were removed from the mixture by steam distillation. There is considerable polymerization during the dehydration and much tarry residue is formed. The ease of polymerization in the case of the product from the unsaturated alcohols may be accounted for by the presence of conjugated double bonds.

TABLE IV

UNSATURATED HYDROCARBONS BY DEHYDRATION OF THE TERTIARY ALCOHOLS

No.	Substance	B. p. (20 mm.), °C.	d_4^0	d_4^{20}
V	1-Methyl-6-cyclohexylidene-Δ'-cyclohexene	130–132	0.9432	0.9282
VI	1-Ethyl-6-cyclohexylidene-Δ'-cyclohexene	139–141	.9461	.9308
VII	1-Ethyl-2-cyclohexyl-cyclohexene	141–143	.9406	.9274

REFRACTIONS, MOLECULAR REFRACTIONS AND ANALYSES

		M		Carbon, %		Hydrogen, %	
No.	*n*	Calcd.	Found	Calcd.	Found	Calcd.	Found
V	1.5165	56.90	56.80	88.57	88.60	11.43	11.37
VI	1.5172	61.52	61.22	88.35	88.37	11.65	11.47
VII	1.5108	61.98	61.53	87.42	87.02	12.58	11.91

Saturated Hydrocarbons

The unsaturated hydrocarbons V and VI were hydrogenated. In both cases 250 cc. of 95% alcohol was used as solvent with 1 g. of the platinum oxide catalyst. For 15.45 g. of Compound V the calculated volume of hydrogen is 3940 cc. while 3910 cc. was taken up, and for 12.7 g. of Compound VI the calculated volume is 3000 cc., and 3000 cc. was absorbed. The rate of absorption dropped markedly when about one-half of the calculated amount had been absorbed. This is probably due to the presence of conjugated double bonds. After complete saturation the catalyst was filtered off and the alcohol removed by distillation. The hydrocarbons

TABLE V

SATURATED HYDROCARBONS

No.	Substance	B. p. (20 mm.), °C.	d_4^0	d_4^{20}
VIII	1-Methyl-2-cyclohexyl-cyclohexane	131–133.5	0.9203	0.9058
IX	1-Ethyl-2-cyclohexyl-cyclohexane	141–142.5	.9240	.9126

REFRACTIONS, MOLECULAR REFRACTIONS AND ANALYSES

		M		Carbon, %		Hydrogen, %	
No.	*n*	Calcd.	Found	Calcd.	Found	Calcd.	Found
VIII	1.4968	57.84	57.55	86.54	86.26	13.46	13.07
IX	1.4964	62.11	62.44	86.51	86.22	13.49	13.37

VIII and IX were further purified by steam distillation, dried over calcium chloride and finally distilled under a vacuum. Treatment with bromine in chloroform solution indicated complete saturation in each case.

Summary

Cyclohexanone has been condensed with *p*-toluic aldehyde, 2,4-dimethyl- and *p*-bromobenzaldehyde. 2,6-Dibenzyl-, dianisyl-, dipiperonyl-, di-*p*-tolylyl-, di(2,4,-dimethyl)benzyl- and di-*p*-chlorobenzyl-cyclohexanones have been obtained by hydrogenating the corresponding unsaturated ketones.

Tertiary alcohols have been prepared by the action of the Grignard reagent on cyclohexylidene-cyclohexanone. These have been hydrogenated. The saturated and the unsaturated tertiary alcohols have been dehydrated and the unsaturated hydrocarbons have been hydrogenated.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

STUDIES ON THE DIRECTIVE INFLUENCE OF SUBSTITUENTS IN THE BENZENE RING. III. THE ACTIVE AGENT IN AQUEOUS BROMINATION[1]

BY A. W. FRANCIS[2]

RECEIVED APRIL 14, 1925 PUBLISHED SEPTEMBER 5, 1925

Bromination in aqueous solution is usually considered to be due to the presence of hypobromous acid,[3,4] since it is very much faster than bromination in anhydrous media. The idea is further favored and even considered proved[4] by the fact that aqueous bromination is markedly slower in the presence of large amounts of acid, especially hydrobromic acid, these being the conditions for extremely low concentrations of hypobromous acid. Furthermore, saturation of ethylenic bonds with bromine water frequently gives considerable amounts of bromohydrin compounds.[5]

There are, however, certain considerations which throw doubt upon the assumption that hypobromous acid is the only, or even the principal active agent in aqueous bromination. Some of these appeared in connection with the work described in Part II.[6]

[1] Presented in part at the Sixty-ninth Meeting of the American Chemical Society, Baltimore, April, 1925.

[2] National Research Fellow in Chemistry.

[3] Stark, *Ber.*, **43**, 670 (1910).

[4] Baines, *J. Chem. Soc.*, **121**, 2810 (1922).

[5] Read and others, *J. Chem. Soc.*, **101**, 760 (1912); **111**, 240 (1917); **117**, 359, 1214 (1920); **119**, 1774 (1921); **121**, 2550 (1922); *J. Proc. Roy. Soc. N. S. Wales*, **51**, 558 (1917).

[6] Francis, Hill and Johnston, THIS JOURNAL, **47**, 2211 (1925).