with an equal volume of an aqueous 1.938% sucrose solution carefully buffered to *p*H 4.4. The copper reduction of the resulting 0.0283 *M* mixture was plotted against time and the unimolecular velocity constants were calculated for 30, 40, 50, 60, 70, 80, and 90% inversion. These constants were, respectively, 5.31, 5.50, 5.31, 4.89, 4.74, 4.72, and 5.39 times greater than those determined at similar stages in the enzymotic hydrolysis of the gamma benzylfructoside mixture. Invertase therefore hydrolyzed a constituent in the latter approximately 5.1 times more slowly than sucrose.

One of the authors (C. B. P.) desires to thank the Chemical Foundation of New York for a Research Associateship.

Summary

1. Crystalline α-methylfructofuranoside, m. p. 80.5–81° and $[\alpha]^{20}_D$ +93.0° in water, gave a new crystalline tetraacetate, m. p. 48–48.5° and $[\alpha]^{20}_D$ +88.1° in chloroform, which was also prepared directly from sucrose.

2. An unstable, amorphous α-methyl glycoside–hydrogen chloride addition compound was precipitated when the constituents were mixed in anhydrous dioxane. The course of the subsequent decomposition was followed in more dilute solution both polarimetrically and by means of the copper reducing power. The behavior of gamma-fructosides dissolved in acid alcohols was in consequence assumed to depend on the formation of reducing, chlorine-containing substances which underwent change prior to their re-condensation with the solvent.

3. α-Methylfructofuranoside, when dissolved in benzyl alcoholic hydrogen chloride, was replaced very rapidly by a mixture of benzyl gamma-fructosides. Pure α-benzylfructofuranoside, m. p. 89°, $[\alpha]^{20}_D$ +45.7° in water, was isolated from this mixture in the form of its crystalline tetraacetate, m. p. 84.5–85°, $[\alpha]^{20}_D$ +64.7° in chloroform. Aqueous acid hydrolyzed the unsubstituted α-benzyl glycoside 16.5 times more rapidly than sucrose but it was unaffected by invertase.

4. Benzyl alcoholic hydrogen chloride partially converted α-benzylfructofuranoside into another non-reducing benzyl derivative of gamma-fructose which was not isolated. This benzyl derivative was hydrolyzed by invertase 5.1 times more slowly than sucrose. It had a specific levorotation of $[\alpha]^{20}_D$ −27 ± 2° in water, calculated on the assumption that it possessed the molecular weight of a true benzylfructoside.

5. The constitutions of the crystalline α-methyl- and α-benzylglycosides described above were established by the methylation method. Tetramethyl α-benzyl- and α-methylfructofuranosides were liquids with refractive indices of n^{19}_D 1.4900 and n^{20}_D 1.4417, respectively, and with specific dextrorotations in chloroform of $[\alpha]^{19}_D$ +83.3° and $[\alpha]^{20}_D$ +115.9°, respectively. Both gave tetramethyl fructofuranose when hydrolyzed with aqueous acid.

6. Fear and Menzies' method of methylation with thallous ethylate and methyl iodide gave satisfactory results in the preparations described in (5).

WASHINGTON, D. C. RECEIVED OCTOBER 2, 1936

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

The Cleavage of Side Chains in Aromatic Hydrocarbons in the Form of Paraffins by Means of Aluminum Chloride[1]

BY V. N. IPATIEFF AND HERMAN PINES

In the course of the study of polymerization of olefins,[2] alkylation[3] and depolyalkylation[4] of aromatic hydrocarbons, one of the chief difficulties in the identification of the reaction products was the lack of an adequate method for determining the structure of the alkyl group attached to the aromatic ring. It was tried[5] by a destructive hydrogenation method to convert the alkyl group to the corresponding paraffinic hydrocarbon. It was possible by this method to obtain methane and benzene from toluene; ethane and benzene from mono- and polyethylbenzene. However, in the case of propyl and butylbenzenes, the alkyl group was decomposed yielding methane, ethane and some propane. The

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[1] Presented before the Division of Organic Chemistry of the American Chemical Society at Pittsburgh, September 7–11, 1936.

[2] Ipatieff and Pines, *J. Ind. Eng. Chem.*, **27**, 1364 (1935); **28**, 684 (1936).

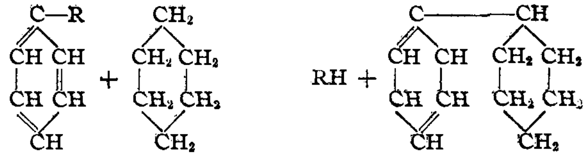
[3] (a) Ipatieff, Pines and Komarewsky, *ibid.*, **28**, 222 (1936); (b) Ipatieff, Corson and Pines, THIS JOURNAL, **58**, 919 (1936); (c) Ipatieff, Komarewsky and Pines, *ibid.*, **58**, 918 (1936).

[4] Ipatieff and Pines, *ibid.*, **58**, 1056 (1936).

[5] Ipatieff and Pines, in publication.

destructive hydrogenation method, therefore, could not be used for the identification of alkylated aromatic hydrocarbons.

During the study of the behavior of different hydrocarbons in the presence of aluminum chloride, it was decided to investigate whether an alkyl group in an alkylated benzene could migrate and attach itself to cyclohexane to give alkylcyclohexane. The migration of alkyl groups from aromatics to naphthenes was not observed to take place. An interesting fact, however, was noticed, namely, when an alkylbenzene is heated with cyclohexane, the alkyl group is split off to yield the corresponding paraffin. Propyl-, *s*-butyl-, *t*-butyl- and *t*-amylbenzene when heated with cyclohexane in the presence of aluminum chloride yield, respectively, propane, butane, isobutane and isopentane. The hydrogen necessary to hydrogenate the alkyl group to the corresponding paraffin comes from the interaction of the two cyclic compounds: aromatic and naphthenic. This could be written schematically as follows



Isopropylbenzene alone does not yield propane under similar conditions; tertiary butylbenzene, however, yields isobutane and high boiling products.

The reaction written above is not the only one which occurs. In the case of isopropylbenzene and cyclohexane, besides propane and phenylcyclohexane, the following products were identified: methylcyclopentane, benzene, *p*-diisopropylbenzene and a product corresponding to cyclohexylisopropylbenzene or methylcyclopentylisopropylbenzene.

The yield of paraffin gases formed from the cleavage of aromatic side chains depends on two factors: (1) the structure of the alkyl group, and (2) the ease with which the cycloparaffin gives off hydrogen.

It was found that the alkyl group of isopropylbenzene splits off with more difficulty in the presence of monosubstituted cyclohexane than in the presence of cyclohexane; disubstituted cyclohexanes such as *p*-methylisopropylcyclohexane do not cause the cleavage of the alkyl groups in isopropylbenzene. Semi-quantitative determinations have shown that the ease of cleaving the isopropyl group from isopropylbenzene decreases with the substitution in the cyclohexane ring.

It was found that decahydronaphthalene facilitates the cleavage of the alkyl group in alkylated benzene. The product obtained from this reaction contains among others a compound corresponding to decahydronaphthylbenzene, which shows the origin of the hydrogen necessary to reduce the alkyl groups to paraffin.

The following tabulation gives the approximate yield of paraffin formed from the reaction between alkylated aromatics with cyclohexane and decahydronaphthalene.

Aromatic hydrocarbon used	Paraffin formed Kind	Naphthene hydrocarbon used Cyclohexane Yield, %	Naphthene hydrocarbon used Decahydronaphthalene Yield, %
Toluene	None	0	0
Ethylbenzene	None	0	0
Isopropylbenzene	Propane	33	53
s-Butylbenzene	Butane	35	71
t-Butylbenzene	Isobutene	61	94
s-Amylbenzene	Isopentane	60	. .

The above tabulation shows ,that a tertiary butyl group splits off more easily than a secondary butyl group and that the latter splits off still more easily than an isopropyl group. Ethyl and methyl groups do not split off under the same conditions. The relative instability of the alkyl groups attached to the benzene ring is the same as that which we would predict from Kharasch's table of the relative electro-negativity of organic radicals.[6]

The method of cleaving alkyl groups from aromatic hydrocarbons could serve as a means for a direct measurement of the relative stability of the bond between the alkyl and phenyl radicals in alkylated aromatic hydrocarbons; it would also be possible to determine by this method the effect of different substituents on the relative stability of this bond. This method could also be used for direct measurement of the relative stability of the carbon–hydrogen bond in cyclic compounds like cyclohexane, decahydronaphthalene and possibly in some paraffinic hydrocarbons. By this method it was found that substitution increases the stability of the carbon–hydrogen bond in the cyclohexyl ring. The tabulation given above has also demonstrated that the carbon–hydrogen bond in decahydronaphthalene is less stable than in cyclohexane.

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[6] (a) Kharasch and Grafflin, This Journal, **47**, 1948 (1925); (b) Kharasch and Marker, *ibid.*, **48**, 3130 (1926); (c) Kharasch and Flenner, *ibid.*, **54**, 674 (1932).

An important application of the above mentioned reaction is its use in determining the structure of alkyl groups attached to an aromatic nucleus. It is important to keep the temperature of the reaction below 80°, since at higher temperatures partial decomposition of the hexamethylene ring to isobutane takes place.

It is worth while to mention here that alkylated cyclohexane when treated under similar conditions with cyclohexane or benzene does not yield paraffinic hydrocarbons. It seems that alkyl groups are much more strongly attached to a hexamethylene ring than to a phenyl ring.

In order to split the side chains from alkylnaphthenes, it is necessary to raise the temperature to 90° or higher; under these conditions, however, the hexamethylene ring decomposes, yielding isobutane.

The same type of reaction as mentioned above takes place when olefins are treated with benzene in the presence of cyclohexane or decahydronaphthalene and aluminum chloride. It seems that alkylation of aromatic hydrocarbons takes place first, which in the presence of cyclohexane dealkylate to give paraffins. *n*-Butene under these conditions yielded *n*-butane, while diisobutene or di-*n*-butene yielded isobutane. The last two experiments show that under these conditions depolyalkylation has taken place. In the case of di-*n*-butene, the depolyalkylation was accompanied by isomerization. The detailed results obtained from the action of olefins on cyclic hydrocarbons will be reported in another paper.

The reactions described in this paper are intended to be studied with other alkylating and polymerizing catalysts.

Apparatus and Procedure.—The apparatus consisted of a 250-cc. flask provided with a dropping funnel, mercury sealed stirrer, reflux condenser and an inlet tube for the hydrogen chloride. Ground glass joints were used throughout. The gases formed were collected in a calibrated trap (100-cc. capacity) cooled to −78° by means of a mixture of carbon dioxide and acetone. The non-condensable gases, if any, were collected in a gas bottle over salt water.

Aluminum chloride and the naphthene or decahydronaphthalene were placed in the flask, and a stream of nitrogen was passed to sweep out the air; a slow stream of hydrogen chloride was passed in and the flask was heated to the desired temperature by means of a water-bath. The aromatic hydrocarbons were then introduced. The gases evolved were submitted to a fractional distillation in a low temperature Podbielniak apparatus. The contents of the flask after the reaction consisted, in most cases, of two layers; the upper hydrocarbon layer was washed with 10% solution of sodium hydroxide followed by water, dried over calcium chloride and distilled. The lower aluminum chloride layer was decomposed with ice, neutralized with sodium hydroxide solution, dried and distilled.

Materials.—Toluene, xylenes, ethylbenzene and cyclohexane were obtained from the Eastman Kodak Company.

Isopropylbenzene, *s*-butylbenzene, *t*-butylbenzene and *s*-amylbenzene were obtained by treating propene, *n*-butene, isobutene and isopropylethylene, respectively, with benzene using 96% sulfuric acid as the catalyst.[7] In the case of alkylation of benzene with the last two olefins, the chief product formed was the dialkylbenzene which was dealkylated to the mono-substituted benzene by treating it with benzene in the presence of ferric chloride.[8] The aromatic hydrocarbons used had the following boiling ranges and indices of refraction:

Hydrocarbon	B. p., °C.	n^{20}_D
Isopropylbenzene	151–152	1.4922
s-Butylbenzene	170–171	1.4901
t-Butylbenzene	168–169	1.4912
s-Amylbenzene	188–190	1.4932

Decahydronaphthalene was obtained from the Eastman Kodak Co. This product was stable toward a nitrating mixture, indicating the absence of naphthalene or tetrahydronaphthalene. The product was redistilled several times and the fraction having a boiling range of 187–189° and index of refraction n^{20}_D of 1.4745 was used for the reaction.

Isopropylcyclohexane and *p*-methylisopropylcyclohexane were obtained by hydrogenating the corresponding aromatic hydrocarbons under pressure in the presence of nickel.

Experimental Data.—The conditions under which the experiments were carried out and the results obtained are given in Table I.

As an example of the type of products which are obtained, two experiments will be discussed in detail.

Experiment No. 4. Isopropylbenzene-Cyclohexane-Aluminum Chloride-Hydrogen Chloride. Hydrocarbon Layer.—The boiling range of the hydrocarbon layer was as follows:

B. p., °C.	% by weight
76–80	54
150–200	14
200–250	20
250–285	8
Above 285	3

The different products were redistilled and the following fractions isolated.

Fraction 76–80° contains 13.5% of benzene. This was determined by treating the fraction with fuming sulfuric acid (15% SO_3). The remaining compounds consisted of cyclohexane with pure methyl cyclopentane.

Fraction 140–166°, n^{20}_D 1.4909, was completely soluble in 15% fuming sulfuric acid. This indicates the absence of alkyl cyclohexane.

Fraction 202–204°, n^{20}_D 1.4907, corresponds to *p*-diisopropylbenzene. Calcd. for $C_{12}H_{18}$: C, 88.89; H, 11.11; mol. wt., 161. Found: C, 88.77; H, 11.18; mol. wt., 162.

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[7] Ipatieff, Corson and Pines, This Journal, **58**, 919 (1936).

[8] Ipatieff and Corson, unpublished results.

TABLE I

Expt. no.	Aromatic hydrocarbons used	Am., g.	Cyclohexane, g.	$AlCl_3$	Conditions of reactions		Results				
					Temp., °C.	Time, hrs.	Gas found			Hydroc. layer	$AlCl_3$ layer
							cc.	Kind	%		
1	Toluene	55	75	25	67–82	4:15	[a]			51.8	102
2	Xylene	48.5	57.5	25	67–80	3:15	[a]			84.6	96.7
3	Ethylbenzene	48	57	23	70–80	3:25	[a]			75.7	97.8
4	Isopropylbenzene	36	37.8	10	80	3:00	2400	Propane	96	51.5	27.5
5	*p*-Diisopropylbenzene	48.6	54.3	15	80	3:15	2600	Propane	96	79.1	31.2
6	*s*-Butylbenzene	40	38	10	80	3:00	2300	*n*-Butane	100	51.8	25.7
7	*t*-Butylbenzene	40	38	10	70	1:00	4000	*i*-Butane	100	..	..
8	*s*-Amylbenzene	44	38	15	65–82	2:00	Liq. 17 cc.	*i*-Pentane	100	40.9	40.4
			Decahydronaphthalene								
9	Isopropylbenzene	36	62	15	80	3:00	3610	Propane	98	69.7	37.0
10	*s*-Butylbenzene	40	62	15	80	3:00	4790	*n*-Butane	98	69.4	38.6
11	*t*-Butylbenzene	40	62	15	60–78	1:15	6450	*i*-Butane	98	57.9	46.4

[a] Negligible amount of methane and ethane was formed.

The oxidation of the fraction by means of dilute nitric acid (1:2.5) yielded terephthalic acid, which when converted to dimethyl terephthalate yielded a crystalline product with a melting point of 138°.

Fraction 239–245°, n^{20}_D 1.5191, probably contains a mixture consisting of triisopropylbenzene and phenylcyclohexane or phenylmethylcyclopentane. Calcd. for C_6H_5-C_6H_{11}: C, 90.0; H, 10.0; mol. wt., 184; n^{20}_D, 1.5275. Calcd. for $C_6H_3(C_3H_7)_3$: C, 87.9; H, 12.1; mol. wt., 204; n^{20}_D, 1.4929. Found: C, 89.3; H, 10.42; mol. wt., 174. On the basis of organic analysis and molecular weight determinations and index of refraction, it seems that the product consists of a mixture composed of 30% triisopropylbenzene and 70% of phenylcyclohexane.

Use of the dehydrogenation method, conversion of phenylcyclohexane to diphenyl is contemplated for proving the presence of the latter.

Fraction 275–280°, n^{20}_D 1.5170, corresponds to isopropylcyclohexylbenzene. Calcd. for $C_3H_7C_6H_4C_6H_{11}$: C, 89.11; H, 10.89; mol. wt., 202. Found: C, 89.19; H, 10.92; mol. wt., 207.

Catalyst Layer.—The aluminum chloride layer after being decomposed, washed and dried, weighed 11 g. It was submitted to a fractional distillation.

B. p., °C.	% by weight
75–78	27
78–148	6
148–250	19
250–315	21
315–360	10
Above 360	12

The index of refraction of the different fractions corresponded very closely to the index of refraction of the hydrocarbon layer.

Fraction 275–285°, n^{20}_D 1.5232, corresponds to isopropylcyclohexylbenzene. Calcd. for $C_3H_7C_6H_4C_6H_{11}$: C, 89.11; H, 10.89; mol. wt., 202. Found: C, 89.50; H, 10.42; mol. wt., 206.

Experiment 11. *t*-Butylbenzene-Decahydronaphthalene-Aluminum Chloride-Hydrogen Chloride. Hydrocarbon Layer.—After washing and drying it weighed 51.05 g. The following is the distillation range of the product.

B. p., °C.	% by weight
82–94	9.6
94–160	1.5
160–200	54.5
200–250	6.0
250–320	20.0
Bottoms	8.4

On redistillation the several fractions were separated.

Fraction 82–94° consisted of benzene.

Fraction 185–190°, n^{20}_D 1.4697, stable toward a nitrating mixture; organic analysis shows that it corresponds to decahydronaphthalene. Calcd. for $C_{10}H_{18}$: C, 86.97; H, 13.04; mol. wt., 138. Found: C, 87.14; H, 13.14; mol. wt., 136.

The index of refraction of this fraction was lower than that of the original product. This indicates that isomerization has taken place. Whether this is the case of *cis-trans* isomerization or whether the six-membered rings isomerize into five-membered rings as in the case of cyclohexane, is being investigated.

Fraction 300–310°, n^{20}_D 1.5330. This product corresponds to decahydronaphthylbenzene. Calcd. for $C_{10}H_{17}$-C_6H_5: C, 89.72; H, 10.28; mol. wt., 214. Found: C, 89.38; H, 10.62; mol. wt., 205; d^{20}_4, 0.9696.

Aluminum Chloride Layer.—The catalyst layer was decomposed, washed, dried and distilled.

B. p., °C.	% by weight
80–90	10.5
90–180	5.0
180–230	15.5
230–330	7.4
Bottoms	62.1

The product was redistilled and the index of refraction of the different fractions is the same as for the corresponding ones of the upper layer.

Acknowledgment.—The authors thank Mr. Bruno Kvetinskas for assistance in the experimental work.

Summary

When alkylbenzenes are heated with cyclohex-

ane or decahydronaphthalene in the presence of aluminum chloride catalyst, the alkyl groups are split off to yield the corresponding paraffins.

The relative stability of different alkylbenzenes is reported.

Various applications of this reaction are proposed.

RIVERSIDE, ILL. RECEIVED OCTOBER 5, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Thermal Decomposition of Gaseous Silicon Tetramethyl

BY DAVID F. HELM AND EDWARD MACK, JR.

In a previous paper[1] a study was made of the thermal decomposition of gaseous germanium tetraethyl. In the present paper the same type of study has been made of silicon tetramethyl. We have found that silicon tetramethyl gives a homogeneous decomposition which is unimolecular down to pressures of about 10 cm. In the case of germanium tetraethyl, over the temperature range employed, 420–450°, the products of the decomposition were a bright mirror-like deposit of germanium on the walls of the reaction vessel and a gas phase of essentially the same composition as the products obtained from the pyrolysis of *butane* at these temperatures. Whereas in the case of the more stable silicon tetramethyl it was necessary, to obtain a conveniently measurable rate of decomposition, to work at a much higher temperature, 660–720°, a sooty deposit was formed, consisting of silicon *and carbon*, and the gaseous products resembled closely those obtained from the pyrolysis of *ethane* at these temperatures.

Experimental

Silicon tetramethyl was prepared with the Grignard reaction by a method analogous to that employed[2] by Dennis and Hance for making germanium tetramethyl. The fraction of the purified product saved for use had a boiling point of 26.30 ± 0.05°.

The course of the decomposition was followed by three different manometer techniques, all of which gave substantially the same results. These included (1) a direct manometric method which was later abandoned in favor of (2) pointer membrane manometers and (3) clicker type null pressure gages. The pointer manometers were used in the same way as those described by Geddes[1] and Mack. Clicker gages were mounted outside the furnace and connected to the reaction vessel and the manometer line in the usual manner.

In the fairly high temperature range, 660–720°, it was necessary that fuzed quartz reaction chambers be used rather than Pyrex. Constant temperature inside a heavily lagged electric furnace was maintained within 0.3° with a platinum resistance thermometer wound near the heating coils and with an automatic controlling mechanism similar to that described by Scott and Brickwedde.[3]

Treatment of Data

The data for a typical run (No. 33) are given in Table I. This decomposition was carried

TABLE I

DATA FOR VELOCITY CONSTANT AT 678.7°

Time, min.	Pressure (P), cm.	$P_\infty - P$	k, sec.$^{-1}$	
Before	10.35			
0	33.00 = P_0			
3.62	38.35	58.45		
4.55	42.30	54.50	0.00126	
5.28	45.70	51.10	.00147	
6.00	48.64	48.16	.00137	
7.03	52.60	44.20	.00139	
7.92	55.70	41.10	.00137	
9.07	59.35	37.45	.00135	Av. 0.00133 0.4 to 0.8 completed
10.02	62.13	34.67	.00135	
11.25	65.45	31.35	.00136	
12.48	68.37	28.43	.00132	
13.75	71.10	25.70	.00133	
14.92	73.35	23.45	.00131	
16.07	75.45	21.35	.00136	
17.50	77.73	19.07	.00131	
19.35	80.32	16.48	.00132	
20.65	81.91	14.89	.00130	
22.08	83.50	13.30	.00132	
23.55	84.95	11.85	.00131	
25.17	86.40	10.40	.00134	
27.20	87.90	8.90	.00128	
28.62	88.85	7.95	.00132	
31.05	90.22	6.58	.00130	
33.12	91.20	5.60	.00129	
37.08	92.66	4.14	.00127	
42.06	94.05	2.75		
92.00	96.80 = P_∞			
After run	31.15	$P_\infty/P_0 = 2.95$		

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(1) Geddes and Mack, THIS JOURNAL, 52, 4372 (1930).

(2) Dennis and Hance, *J. Phys. Chem.*, 30, 1055 (1926).

(3) Scott and Brickwedde, *Bur. Standards J. Research*, 6, 407 (1931).