[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Study in the Terpene Series. XXII.[1a] Synthesis, Physical Constants and Catalytic Dehydrogenation of 1-Methyl-1-ethyl-, 1-Methyl-1-*n*-propyl- and 1-Methyl-1-isopropylcyclohexane[1b]

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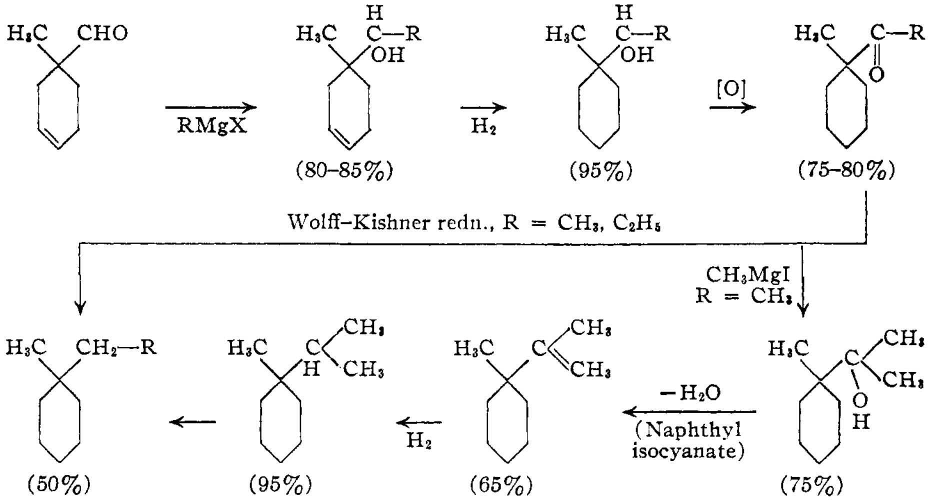
1-Methyl-1-ethyl-, 1-methyl-1-*n*-propyl- and 1-methyl-1-isopropylcyclohexane have been synthesized starting with 4-methyl-4-formylcyclohexane, which was obtained by the Diels–Alder condensation of 1,3-butadiene and methacrolein. Physical constants of the hydrocarbons and of their intermediates have been determined. Infrared spectra of the hydrocarbons are given. The dehydrogenation studies of these hydrocarbons were made at 330° using platinum–alumina and at 500° using chromia–alumina as catalysts. In the presence of chromia–alumina catalyst toluene was the main product of reaction as a result of the removal of the higher alkyl groups. In the presence of the platinum–alumina catalyst, the reaction was not too specific, and there was no selectivity in the removal of alkyl groups.

Substituted cyclohexanes containing a geminal carbon atom were often encountered during the study of terpenes and related hydrocarbons.[2] Since the structure of these hydrocarbons was determined by means of dehydrogenation which involved the removal of one of the geminal alkyl groups, it was of interest to investigate which of the alkyl groups is preferentially removed in such a dehydrogenation. For that reason the dehydrogenation of compounds having a methyl and a higher alkyl group attached to the same atom of the cyclohexane ring was studied. The hydrocarbons chosen were: 1-methyl-1-ethyl, 1-methyl-1-*n*-propyl- and 1-methyl-1-isopropylcyclohexane. Platinum–alumina and chromia–alumina were used. These catalysts were found previously to be effective for the dehydrogenation of alkylcyclohexanes containing a geminal carbon atom.[3]

Synthesis of Geminal Alkylcyclohexanes.—1-Methyl-1-ethyl, 1-methyl-1-*n*-propyl- and 1-methyl-1-isopropylcyclohexane were synthesized starting with 1,3-butadiene and methacrolein, according to the scheme.

The alcohols formed from the above outlined reactions could exist as mixtures of diastereomers rather than pure substances. It was found, however, that alcohols I, II and V (Table I) formed solid 2,4-dinitrobenzoates in good yields and with sharp melting points after a second crystallization from ethanol. This indicates that a single diastereomer predominates.



Alcohol IV gave an oily product from which an impure dinitrobenzoate was prepared, which did not have a sharp melting point. Alcohol VI did not form a dinitrobenzoate. The dehydration of the saturated alcohols, as an intermediate step, was also investigated, using alumina as a catalyst. It was found, however, that skeletal isomerization accompanied this reaction. A similar type of skeletal isomerization was reported previously when alcohol II was treated with zinc chloride.[4] The olefins resulting from such dehydration were composed of an equal mixture of 1,2-dimethyl-1-cycloheptene and 1-isopropyl-1-cyclohexene. In order to avoid this isomerization the dehydration of 1-(1-methylcyclohexyl)-propanol to the corresponding olefin was achieved through the use of α-naphthyl isocyanate. This method was similar to the one described previously where phenyl isocyanate was used as a dehydrating agent.[5] The use of α-naphthyl isocyanate was preferred in this particular case due to the differences in boiling points of this compound and the olefin resulting from the dehydration.

In the course of the synthesis of the geminal dialkylcyclohexanes several new compounds were pre-

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[1a] For previous paper of this series see: H. Pines and N. E. Hoffman, THIS JOURNAL, **76**, 4417 (1954).

[1b] Presented in part before the Division of Petroleum Chemistry at the 126th Meeting of the American Chemical Society, New York, September, 1954.

[1c] On leave of absence from: "Laboratoires de Recherches Purfina S.A." Bruxelles, Belgium.

(2) (a) H. Pines and J. Ryer, unpublished results presented partly before the Petroleum Division, 125th A.C.S. Meeting, Kansas City, Missouri, March, 1954; (b) V. N. Ipatieff, F. J. Pavlik and H. Pines, THIS JOURNAL, **75**, 3179 (1953).

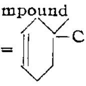
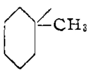
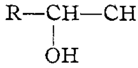
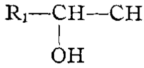
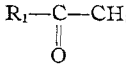
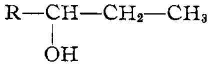
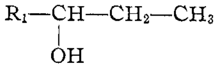
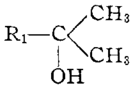
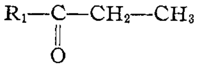
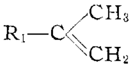
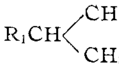
(3) H. Pines, E. F. Jenkins and V. N. Ipatieff, *ibid.*, **75**, 6226 (1953).

(4) H. Meerwein and J. Schäfer, *J. prakt. Chem.*, **104**, 289 (1922).

(5) H. Pines, W. D. Huntsman and V. N. Ipatieff, THIS JOURNAL **75**, 2215 (1953).

TABLE I

PHYSICAL CONSTANTS OF GEMINAL DIALKYLCYCLOHEXANES AND OF THEIR INTERMEDIATES

Compound R =  R_1 = 	Number	Boiling point[b] Temp., °C.	Boiling point[b] Pressure, mm.	d^{20}_4	n^{20}_D	MR_D[c] Calcd.	MR_D[c] Obsd.
 $R\text{—}CH(OH)\text{—}CH_3$	I[a]	136.7	100	0.95651	1.4858	42.62	42.07
 $R_1\text{—}CH(OH)\text{—}CH_3$	II	134.9	100	.93137 (.9312)[3]	1.4716 (1.47203)[3]	43.09	42.73
 $R_1\text{—}CO\text{—}CH_3$	VIII	120.0	100	.91785 (.9178)[3]	1.4547 (1.45484)[3]	41.57	41.42
 $R\text{—}CH(OH)\text{—}CH_2\text{—}CH_3$	IV[a]	148.3	100	.95044	1.4840	47.24	46.43
 $R_1\text{—}CH(OH)\text{—}CH_2\text{—}CH_3$	V[a]	146.1	100	.92784	1.4711	47.70	47.08
 $R_1\text{—}C(OH)(CH_3)CH_3$	VI[a]	144.3	100	.93929	1.4776	47.70	47.06
 $R_1\text{—}CO\text{—}CH_2\text{—}CH_3$	VII[a]	134.7	100	.91490	1.4553	46.19	45.77
$R_1\text{—}CH_2\text{—}CH_3$	VIII	151.8 (151.1-151.3)[6]	760	.80652	1.4414 (1.4418)[6]	41.56	41.37
$R_1\text{—}CH_2\text{—}CH_2\text{—}CH_3$	IX	174.3 (174.3)[6]	760	.81008	1.4440 (1.4455)[6]	46.18	45.99
 $R_1\text{—}C(CH_3)\text{=}CH_2$	X[a]	172.3	760	.84475	1.4630	45.71	45.07
 $R_1CH(CH_3)CH_3$	XI[a]	177.5	760	.82615	1.4512	46.18	45.73

[a] These compounds apparently have not been described previously in the literature. [b] A modified Cottrell apparatus was used.[7] [c] For all the compounds observed, the molecular refraction is lower than the calculated values. The same discrepancy was found previously[8] for a series of compounds containing a quaternary carbon atom.

pared and their physical constants are summarized in Table I. Their infrared spectra were recorded using a double beam spectrophotometer[6] and are reported in Table II.

Dehydrogenation of Geminal Alkylcyclohexanes.—The dehydrogenation of the 1-methyl-1-alkylcyclohexanes, both in the presence of platinum–alumina and chromia–alumina catalysts, was accompanied by a removal of one of the alkyl groups. In all the experiments the aromatic fractions contained less than 0.5% of benzene. The presence of traces of benzene also was observed when methylcyclohexane was dehydrogenated under experimental conditions similar to that of 1-methyl-1-alkylcyclohexanes. The recovered non-aromatic hydrocarbons consisted of the starting material only. The dehydrogenation proceeded practically without the formation of side reactions, such as migration of alkyl groups. Such a migration has been reported to accompany the dehydrogenation of cyclic saturated hydrocarbons containing a geminal carbon atom.[3,9–12] The dehydrogenation of hydroaromatic derivatives of naphthalene and phenanthrene which carry two alkyl groups on one of the carbon atoms of the nucleus was investigated previously.[11,12] Platinum and nickel were used as catalysts. The following difference in the behavior of both catalysts was found: the platinum-on-charcoal catalyst brought aromatization through elimination of an alkyl group on the quaternary carbon, whereas the nickel–kieselguhr catalyst was found to bring aromatization by migration of an alkyl group. Some compounds containing two different alkyl groups, a methyl and an ethyl or a phenyl group, on the same carbon atom also were dehydrogenated in the presence of nickel catalysts.[11,12] The dehydrogenation was found to be accompanied by the elimination of the largest group.

In the present study it was found that the composition of the aromatic hydrocarbons produced did not depend upon the extent of dehydrogenation. In the presence of low activity platinum–alumina catalyst only 24 and 9%, respectively, of 1-methyl-1-ethyl- and 1-methyl-1-*n*-propylcyclohexane underwent dehydrogenation (experiments 5 and 7). However, the composition of the aromatic hydrocarbons produced was almost the same as in simi-

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(6) Baird Associates, Cambridge, Mass. The spectra of the nondiluted compounds were recorded between 2 and 16 μ, using a NaCl prism. The thickness of the cell was approximately 0.1 mm.

(7) F. R. Buck, *et al.*, *J. Inst. Petroleum*, **34**, 339 (1948).

(8) F. G. Cottrell, THIS JOURNAL, **41**, 721 (1919). The apparatus as modified by Universal Oil Product Company makes possible the determination of the boiling points at reduced pressure using only about 3 ml. of samples.

(9) J. Linsk, THIS JOURNAL, **72**, 4257 (1950).

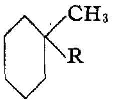
(10) R. P. Linstead, K. O. A. Michaelis and S. L. S. Thomas, *J. Chem. Soc.*, 1139 (1940).

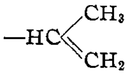
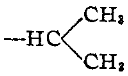
(11) H. Adkins and J. W. Davis, THIS JOURNAL, **71**, 2955 (1949).

(12) H. Adkins and D. C. England, *ibid.*, **71**, 2958 (1949).

TABLE II

INFRARED SPECTRA OF THE HYDROCARBONS



R =	Wave length, μ[a]
—CH_2—CH_3	7.33(s), 7.92(m), 8.02(w), 8.23(w), 8.48(w), 8.67(s), 8.77(s), 9.17(w), 9.42(m), 9.62(m), 10.00(s), 10.42(m), 10.57(s), 10.88(s), 11,39(s), 11.49(s), 11.87(s), 12.94(s)
—CH_2—CH_2—CH_3	7.33(s), 7.95(w), 8.26(w), 8.49(w), 8.67(s), 8.78(s), 9.09(w), 9.28(w), 9.89(w), 10.38(s), 10.78(s), 10.87(s), 11.28(w), 11.46(m), 11.86(s), 12.85(w), 13.55(s)
 $-HC\begin{smallmatrix}CH_3 \\ =CH_2\end{smallmatrix}$	7.35(s), 7.65(w), 7.93(m), 8.14(m), 8.30(m), 8.62(s), 8.77(w), 8.84(w), 8.96(s), 9.10(s), 9.31(m), 9.70(m), 9.87(m), 10.00(w), 10.42(s), 10.63(w), 10.87(m), 11.28(s), 11.69(m), 11.83(w), 12.26(w), 12.51(w), 12.79(w), 13.37(w), 14.07(m)
 $-HC\begin{smallmatrix}CH_3 \\ CH_3\end{smallmatrix}$	7.28(s), 7.40(s), 7.68(w), 7.94(s), 8.23(m), 8.78(s), 9.01(s), 9.27(m), 9.59(m), 9.71(m), 9.88(m), 10.20(w), 10.39(s), 10.54(s), 10.87(m), 11.38(m), 11.74(s), 12.29(w), 12.61(w), 12.84(w)

[a] The peaks are referred to as: (s), strong; (m), medium; and (w), weak.

lar experiments where a more active catalyst was used (experiments 6 and 8).

Chromia–alumina seems to be the more selective of the two catalysts studied. It caused the removal of the largest alkyl group in preference to the methyl group attached to the same carbon atom of the cyclohexane ring. The platinum–alumina catalyst is not too specific for the selective removal of an alkyl group. In the case of 1-methyl-1-isopropylcyclohexane the isopropyl group was removed in preference to the methyl, in a 6-to-4 ratio. The relative removal of ethyl and methyl groups in 1-methyl-1-ethylcyclohexane was about 1-to-1 while the ratio of removal of *n*-propyl to methyl in 1-methyl-1-*n*-propylcyclohexane was about 3 to 7.[13]

The relative ease of the removal of the various alkyl groups is not due to the difference in the temperature at which the dehydrogenation was carried out but to the nature of the two catalysts. It was found in an experiment made in the presence of chromia–alumina catalyst at 430° that the composition of the aromatic hydrocarbons was the same as that at 500° although the extent of dehydrogenation at 430° was much lower.

The above results indicate that chromia–alumina and platinum–alumina catalysts, which apparently give the same type of reaction, behave somewhat differently toward dehydrogenation. Such differences in the relative behavior of these catalysts already have been noticed previously. It was observed that 1-methyl-1-phenylcyclohexane yields methane and biphenyl when dehydrogenated over chromia–alumina catalyst.[14,15] However, in the presence of platinum–alumina catalyst skeletal isomerization occurred and the products of dehydrogenation seemed to be 2-methylbiphenyl.[9] This difference in behavior of the two catalysts was noticed also in the dehydrogenation study of 1,1,3-trimethylcyclohexene.[3] This compound, when passed over chromia–alumina catalyst, yielded only *m*-xylene. In the presence of platinum–alumina, however, the dehydrogenation yielded trimethylbenzenes besides *m*-xylene, which indicates that skeletal isomerization took place.

On the basis of the present investigation and the results previously reported in the literature it can be concluded that chromia–alumina catalyst appears to be more applicable than platinum–alumina for the determination of the structures of cyclohexanes containing a geminal carbon atom.

Experimental

Synthesis of Geminal Alkylcyclohexanes. 4-Methyl-4-formylcyclohexene.—This compound was prepared by a previously described method.[16]

1-(1-Methyl-3-cyclohexenyl)-ethanol (I).—This alcohol was synthesized by treating 1.5 moles of 4-methyl-4-formylcyclohexene with 1.5 moles of methylmagnesium iodide. The complex was decomposed partially by diluted hydrochloric acid until the solution was almost neutral. Ammonium chloride was used to complete the decomposition. The alcohol, obtained in 80% yield, had the following boiling points: 85.8 at 10, 99.4 at 20, 114.3 at 40, 124.0 at 60, 131.1 at 80 and 136.7° at 100 mm.

Anal. Calcd. for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.61; H, 11.14.

The 3,5-dinitrobenzoate, recrystallized from ethanol, melted at 97°.

Anal. Calcd. for $C_{16}H_{18}O_6N_2$: C, 57.48; H, 5.43. Found: C, 57.35; H, 5.42.

1-(1-Methylcyclohexyl)-ethanol (II).—The alcohol I was hydrogenated at 50–60° in a rotating autoclave in presence of nickel–kieselguhr catalyst. The initial pressure was 120 atmospheres. The saturated alcohol II thus obtained had the following boiling points: 84.7 at 10, 98.4 at 20; 113.3 at 40, 122.4 at 60, 129.4 at 80 and 134.9° at 100 mm. It was found 89.4° at 13 mm. by interpolation; reported[3] 87.5° at 13 mm.

Anal. Calcd. for $C_9H_{18}O$: C, 75.99; H, 12.76. Found: C, 75.89; H, 12.45.

The 3,5-dinitrobenzoate, recrystallized from ethanol, melted at 106°.

Anal. Calcd. for $C_{16}H_{20}O_6N_2$: N, 8.33. Found: N, 8.82.

Methyl 1-Methylcyclohexyl Ketone (III).—This ketone was prepared by oxidizing alcohol II, 1.1 moles, with chromic acid according to a previously described method.[17,18] The ketone III which was obtained in 80% yield had the following boiling points: 101.7 at 50, 120.0 at 100, 131.8 at 150 and 140.4° at 200 mm. The boiling point at 760 mm., 186.2°, was found by extrapolation; reported[3] 186.5–187° at 760 mm.

Anal. Calcd. for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.41; H, 11.58.

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(13) It was reported recently [S. I. Chromov, E. S. Balenkova and B. A. Kazanski, *Doklady U.S.S.R.*, **96**, 95 (1954)] tha thte dehydrogenation of 1-methyl-1-ethylcyclohexane in the presence of platinized carbon yielded 37% toluene, 43% of ethylbenzene, 13% of *o*- and 7% of *m*-xylene. No definite proof of structures was given to show that the latter two compounds were xylenes and not *o*- and *m*-ethyltoluene, which might have been formed through a migration of an alkyl group.

(14) V. N. Ipatieff, H. R. Appell and H. Pines, THIS JOURNAL, **72**, 4260 (1950).

(15) V. N. Ipatieff, E. E. Meisinger and H. Pines, *ibid.*, **72**, 2772 (1950).

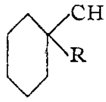
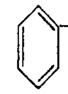
(16) H. Pines, F. J. Pavlik and V. N. Ipatieff, *ibid.*, **73**, 5738 (1951).

(17) H. Pines, A. Edeleanu and V. N. Ipatieff, *ibid.*, **67**, 2193 (1945).

(18) H. Pines, G. Czajkowski and V. N. Ipatieff, *ibid.*, **71**, 3798 (1949).

TABLE III

DEHYDROGENATION OF GEMINAL DIALKYLCYCLOHEXANES

Experiment		1	2	3	4	5	6	7	8	9
Compound[a] 	R =	Ethyl	*n*-Propyl	*i*-Propyl	*n*-Propyl	Ethyl	Ethyl	*n*-Propyl	*n*-Propyl	*i*-Propyl
Catalyst[b]		Chromia–alumina				Platinum–alumina				
Temp., °C.		500			430	330				
Extent of dehydrog., %		90	87	44	22	24[e]	62	9[e]	63	77
Compn. of the gases, mole %[f]	H_2	72.6	71.8	77.2	81.4	73.6	72.0	83.0	75.9	72.7
	CH_4	5.4	6.8	4.5	4.8	12.6	14.8	11.4	17.0	10.5
	C_2H_6	22	..	..	..	13.8	13.2	..	..	..
	C_3H_8	..	21.4	18.3	13.8	..	..	5.6	7.1	16.8
Compn. of the aromatics, mole %[c,d]										
Toluene		80	75	80	74	52	47	32	29	61
	R =	Ethyl	*n*-Propyl	*i*-Propyl	*n*-Propyl	Ethyl	Ethyl	*n*-Propyl	*n*-Propyl	*i*-Propyl
		20	25	20	26	48	53	68	71	39

[a] About 0.05 mole of material was used in each experiment. [b] The reaction tube contained 20 ml. of catalyst, the hourly liquid space velocity was 0.2–0.3. [c] Based on the gas analysis data. [d] Traces of benzene, amounting to less than 0.5% of the aromatics, were found in all the experiments. [e] Catalyst of low activity was used. [f] Calculated on air free basis.

The 2,4-dinitrophenylhydrazone, after recrystallization from ethanol, melted at 132°.

Anal. Calcd. for $C_{15}H_{20}O_4N_4$: N, 17.49. Found: N, 17.73.

The semicarbazone, recrystallized from ethanol, melted at 187°, reported[3] 186°.

1-(1-Methyl-3-cyclohexenyl)-propanol (IV).—This alcohol was synthesized in 85% yield by treating 1.5 moles of 4-methyl-4-formylcyclohexene with 1.5 moles of ethylmagnesium bromide. The alcohol IV had the following boiling points: 124.3 at 40, 134.95 at 60, 142.4 at 80 and 148.3 at 100 mm.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.39; H, 11.08.

An attempt to prepare the 3,5-dinitrobenzoate was not successful.

1-(1-Methylcyclohexyl)-propanol (V).—This alcohol was produced by hydrogenating alcohol IV at 80–90° in a rotating autoclave in presence of nickel–kieselguhr and at an initial hydrogen pressure of 125 atmospheres. The following boiling points were found for the alcohol: 123.2 at 40, 133.1 at 60, 140.5 at 80 and 146.1° at 100 mm.

Anal. Calcd. for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 77.02; H, 12.60.

The 3,5-dinitrobenzoate, recrystallized from ethanol, melted at 92°.

Anal. Calcd for $C_{17}H_{22}O_6N_2$: C, 58.27; H, 6.33. Found: C, 57.69; H, 6.07.

2-(1-Methylcyclohexyl)-2-propanol (VI).—Alcohol VI was obtained in 75% yield by treating ketone III, 0.8 mole, with methylmagnesium iodide. It had the following boiling points: 120.4 at 40, 131.2 at 60, 138.6 at 80 and 144.3° at 100 mm.

Anal. Calcd. for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.34; H, 12.73.

The 3,5-dinitrobenzoate could not be obtained.

Ethyl (1-Methylcyclohexyl) Ketone (VII).—This ketone was made in 75% yield starting with 0.62 mole of V and using the same method as described for the preparation of III. The boiling points of VII are as follows: 115.3 at 50, 134.7 at 100, 147.3 at 150 and 157.5° at 200 mm.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.88; H, 11.59.

The 2,4-dinitrophenylhydrazone, recrystallized from ethanol, melted at 78.5°.

Anal. Calcd. for $C_{16}H_{22}O_4N_4$: N, 16.76. Found: N, 17.15.

1-Methyl-1-ethylcyclohexane (VIII).—This hydrocarbon was synthesized by means of a Wolff–Kishner reduction of 0.57 mole of the ketone III. The reduction was made according to the general procedure of Huang-Minlon,[19] slightly modified.[16] The 1-methyl-1-ethylcyclohexane thus produced was distilled on a "Hypercal" column.[20] The yield was 50%. The synthesis of VIII also was attempted through dehydration of the alcohol II, at 400°, using alumina as a catalyst. The resulting product was hydrogenated at 120 atmospheres and 60°, using nickel–kieselguhr as a catalyst. The infrared spectrum of the saturated hydrocarbon thus obtained was compared with that of the hydrocarbon VIII made by the Wolff–Kishner reduction of the ketone III. The general characteristics of the spectra of both compounds were very similar, but the hydrocarbon obtained through the dehydration process contained additional absorption bands. It was estimated that it was 90–95% pure as compared with the one obtained from the Wolff–Kishner reduction. The physical constants were also different: d^{20}_4 0.80614, n^{20}_D 1.4418; b.p. 152.8° at 760 mm.

1-Methyl-1-*n*-propylcyclohexane (IX).—This hydrocarbon was prepared by the same method as used for VIII. Starting with 0.93 mole of the ketone VII a 50% yield of IX was obtained.

1-Methyl-1-isopropenylcyclohexane (X).—This olefin was produced by a dehydration method. Alcohol VI, 0.59 mole, was mixed with 0.9 mole of α-naphthyl isocyanate. The mixture was stirred and heated. At 160°, the solution became orange, a strong evolution of gas occurred and the mixture became solid. The temperature was raised to 200° and the olefin removed under reduced pressure. The olefin was distilled on a "Hypercal" column.[12] The yield was 65%.

Anal. Calcd. for $C_{10}H_{18}$: C, 86.87; H, 13.13. Found: C, 87.17; H, 12.97.

1-Methyl-1-isopropylcyclohexane (XI).—This hydrocarbon was prepared by hydrogenating olefin XI under pressure, at 80–90°, in a rotating autoclave and in the presence of nickel–kieselguhr catalyst.

Anal. Calcd. for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 86.09; H, 14.57.

Dehydrogenation. Procedure.—The dehydrogenation experiments were made at atmospheric pressure, following a previously described method.[3]

The gases obtained from the dehydrogenation were analyzed on a mass spectrograph. The liquid products were fractionated on a Piros–Glover spinning band column[21] and each fraction was examined by infrared spectrophotometry.[6] The results are summarized in Table III. The composition of the aromatic hydrocarbons which were formed was determined from the infrared spectral analysis and from the gas analysis data. Both methods were in good agreement with

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(19) Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

(20) Podbielniak, Inc., Chicago, Ill.

(21) Manufactured by H. S. Martin and Co., Evanston, Ill.

each other. The catalysts were: platinum–alumina containing 7% of platinum,[22] and chromia–alumina promoted with cerium and potassium.[23]

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EVANSTON, ILLINOIS

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[CONTRIBUTION FROM THE NAVAL STORES STATION, U. S. DEPARTMENT OF AGRICULTURE[1]]

The Isolation of a New Resin Acid from Gum Rosin—Palustric Acid

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A new primary acid of the abietic type, named palustric acid, has been isolated from gum rosin by means of partition chromatography. The presence of this acid in the oleoresin of *Pinus palustris* and *Pinus caribaea* has been established. The physical constants and ultraviolet absorption spectrum have been obtained. Palustric acid has been isolated as an intermediate product in the acid and heat isomerization of levopimaric acid to abietic acid.

While a large number of acids have been reported as being present in pine oleoresin and rosin, on further investigation several of these acids have been shown to be mixtures. Only about seven resin acids from these sources have been characterized fully.[2–6] The most successful method for isolation of pure resin acids has been the recrystallization of certain amine salts of the resin acids from suitable solvents.[7,8] Since similar separation problems in fatty acid chemistry had been solved by the application of partition chromatography using an amine as the immobile phase, the method developed by Ramsey and Patterson[9] for the saturated straight-chain fatty acids C_{11} to C_{19} was applied to mixtures of the known resin acids. This technique divided the previously characterized resin acids into four groups (Fig. 1, curve 1). The acids eluted at fraction number 22 were a mixture of di- and tetrahydroresin acids. The second group (peak effluent volume 380–390) contained dextropimaric, isodextropimaric, levopimaric and *l*-abietic acids. Neoabietic acid was the only acid eluted in fractions 47–59 and dehydroabietic acid was the only acid eluted in fractions 61–77.

When rosin and oleoresin were chromatographed by this method, five peaks were obtained which did not correspond to the peaks of previously isolated resin acids (Fig. 1, curve 2). The peak effluent volumes of these unknown acids are 70, 310, 720, 790 and 890. Of these, the acid with a peak effluent volume of 310 has been isolated. On the basis of the ultraviolet spectrum this peak contained between 55 and 70% of an unknown acid which had a characteristic ultraviolet absorption maximum at 265–266 mμ. The other acidic material in this peak had no characteristic ultraviolet absorption and was probably a mixture of dextro- and isodextropimaric acids. The new acid was obtained pure by repeated recrystallization of the acid in fractions 25 through 33 from methanol.

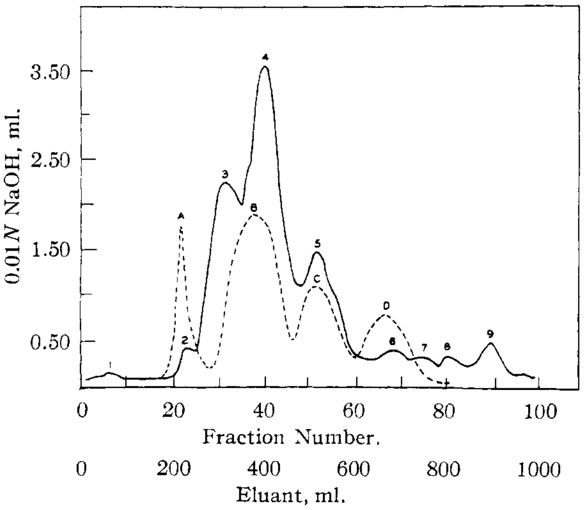

Fig. 1.—Curve 1, - - -; chromatogram of pure resin acids: peak A, di- and tetrahydroresin acids; peak B, dextropimaric acid, isodextropimaric acid, levopimaric acid, *l*-abietic acid; peak C, neoabietic acid; peak D, dehydroabietic acid. Curve 2, ——; chromatogram of WW gum rosin: peak 3, palustric acid.

This new acid was first detected in the oleoresin of *Pinus palustris* and for this reason it was named palustric acid. Since it is present in the pine oleoresin, it is a primary resin acid. Palustric acid has an $[\alpha]_D$ +71.8° (2% EtOH), m.p. 162–167°, and an ultraviolet absorption maximum at 265–266 mμ with a specific absorption coefficient, α, of 30.1 (Fig. 2, curve 1). Palustric acid is an isomerization product of levopimaric acid and on treatment with mineral acid it is isomerized to *l*-abietic acid. It does not react with maleic anhydride at room temperature, but at elevated temperatures it reacts to form an addition product that is identical with the prod-

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[1] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

[2] J. L. Simonsen and D. H. R. Barton, "The Terpenes," Vol. III, Cambridge University Press, 1952, pp. 374–458.

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[6] L. F. Fieser and W. P. Campbell, *ibid.*, **60**, 159 (1938).

[7] S. Palkin and T. H. Harris, *ibid.*, **56**, 1935 (1934).

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