agent of V gave 5.5 g. (45%) of desoxybenzoin, b.p. 160–162° (3 mm.), m.p. 55–57° after one recrystallization from a mixture of benzene and ethanol. The desoxybenzoin was further identified by the mixed melting point method and by conversion to the 2,4-dinitrophenylhydrazone, m.p. 198–199°.

A solution of 0.06 mole of α-trimethylsilylbenzylmagnesium bromide in 200 ml. of ether was poured onto a large excess of Dry Ice and the reaction mixture worked up as usual, yielding 6.6 g. (58%) of benzyltrimethylsilane, b.p. 42–43° (1 mm.), n^{25}D 1.4912. The residue (3.2 g.) consisted of dimer VIII, m.p. 140–145°. No carboxylic acid was found.

In another experiment the ether phase was extracted with 10% sodium bicarbonate, but no acidic product was found.

Cleavage of α-Halosilanes with Basic Reagents.—In Table III are summarized the experimental conditions and results obtained on treating certain α-halosilanes with basic reagents.

Attempted Conversion of Acetate XII and Bromide V to the Carbinol.—Treatment of acetate XII with 12% ethanolic potassium hydroxide solution at 50° produced a vigorous reaction but no pure product could be isolated. Refluxing the methanolic solution of the acetate in the presence of a trace of sulfuric acid failed to produce any change within 6 hours, the acetate being recovered. After 16 hours under these conditions, about 25% of the acetate had been decomposed but the product, b.p. 80–82° (8 mm.), failed to analyze for the corresponding silyl alcohol.

Treatment of bromide V with equivalents of sodium hydroxide (in methanol at 50–55° for 10 hours) and of potassium hydroxide (in absolute ethanol at reflux temperature of one hour) caused decomposition, but the silyl alcohol could not be isolated. Bromide V was recovered (94%) after stirring an ether solution of it with 10% aqueous sodium hydroxide for 9 hours.

DURHAM, NORTH CAROLINA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

Reaction of Alkanes with Hydrogen and Deuterium. Racemization and Exchange

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RECEIVED MARCH 27, 1952

In the presence of a nickel–kieselguhr catalyst and at temperatures of about 90 to 130°, the hydrogen atoms of heptane, (+)3-methylhexane, 3,3-dimethylhexane and 2,2,3-trimethylbutane exchange with deuterium. The relative numbers of molecules exchanged under equivalent conditions decrease in the order listed with a factor of about seven separating the extremes. The relative abundance of the various exchanged species has been determined mass spectrographically. All possible exchanged species are present in the case of the first two hydrocarbons with the more exchanged species weighted much more heavily than corresponds to statistical equilibrium. A maximum of seven exchanged hydrogen atoms is found in the last two. Apparently, the exchange process cannot propagate past a quaternary carbon atom. (+)3-Methylhexane is racemized under the same conditions and at a rate substantially independent of whether hydrogen or deuterium is present. The ratio of the number of molecules which suffer exchange to that racemized is about 1.6. Within the range studied, the rate of racemization is representable by $k_0e^{-26,000/RT}\ p_{\mathrm{H}_2}{}^{-0.6}p_{3\mathrm{MH}}{}^{1/3}$. In the absence of hydrogen the catalyst becomes poisoned. Any mechanism must consider that exchange is apparently accompanied by racemization. Partial reversal of olefin hydrogenation seems a likely mechanism. It must involve, however, a symmetric intermediate.

The development of theories of mechanisms of organic reactions has been greatly facilitated by simultaneous study of the kinetics and the stereochemistry of reactions of optically active compounds. Little application of similar studies has appeared in heterogeneous catalytic processes.

Methane, ethane and propane have been shown to exchange with deuterium in the presence of nickel–kieselguhr catalysts.[1] Determination of whether racemization accompanies exchange when an optically active hydrocarbon is employed and, if so, determination of the relationship between the two reactions seemed of considerable potential value in extending our knowledge of the complex of reactions occurring between hydrogen and hydrocarbons. Accordingly, this paper presents the results of such an investigation employing (+)3-methylhexane and nickel–kieselguhr catalysts.

Experimental Techniques

Materials.—The preparation of (+)3-methylhexane has been described.[2] The heptylene was fractionated in a 50-plate Stedman column and hydrogenated at high pressure (about 100 atm.) at not over 70° with nickel–kieselguhr catalyst. Slight racemization results from this process but it is more convenient than the hydrogenation with platinum oxide formerly employed. In later stages of the present work, washing the resultant hydrocarbon with sulfuric acid before final fractionation was replaced by silica gel percolation. No difference in behavior of the product was observed. The infrared absorption spectrum of every batch was checked against a Bureau of Standards standard sample of 3-methylhexane on a Beckman IR2T infrared absorption spectrograph. Deviations were within 1% in transmission. However, traces of olefin were probably present since the product began to absorb in the ultraviolet at about 2200 Å.

Eastman Kodak Company synthetic *n*-heptane was refractionated and percolated through silica gel. High purity 2,2,3-trimethylbutane was supplied by the General Motors Corporation, Research Laboratories Division. It had been treated with silica gel before use. 3,3-Dimethylhexane was supplied by A.P.I. Research Project 45 at The Ohio State University. Its purity was reported to be 99.1 ± 0.3 mole %.

Nickel–kieselguhr catalyst (Universal Oil Products Company)[3] crushed and sieved to 20–40 mesh was reduced *in situ* with hydrogen. In the earlier experiments, a reduction temperature of 250° was employed. The catalytic activity varied considerably from sample to sample and was not stable for a given sample. After run 104, reduction at 300° was employed. Consistent and stable activity resulted.

Deuterium (99.5%) was obtained from the Stuart Oxygen Company under allocation from the Atomic Energy Commission.

Apparatus.—Tanks of electrolytic hydrogen, deuterium and helium were connected through capillary flow-meters to a manifold. Traps were provided between the flowmeters and the manifold. They were cooled with Dry Ice in the first two cases. With helium, activated charcoal cooled by liquid air was used. Effluent gas from the manifold was passed through a sintered glass bubbler immersed in hydrocarbon. The containing flask was thermostated

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[1] (a) K. Morikawa, W. S. Benedict and H. S. Taylor, THIS JOURNAL, **58**, 1445 (1936); (b) **58**, 1795 (1936); (c) K. Morikawa, N. R. Trenner and H. S. Taylor, *ibid.*, **59**, 1103 (1937).

[2] G. S. Gordon, III, and R. L. Burwell, Jr., *ibid.*, **71**, 2355 (1949).

[3] Reported to contain, when reduced, about 65% nickel, V. N. Ipatieff and B. B. Corson, *Ind. Eng. Chem.*, **30**, 1039 (1938).

by an appropriate vapor-bath. The mixture of gas and hydrocarbon vapor was passed through 2 cc. of catalyst in a tube provided with an internal annular thermocouple well. Glass beads before the catalyst aided in reaching temperature equilibrium. The reactor was surrounded with a thermostatically controlled furnace. Probing with a thermocouple established that variation in temperature within the 25-mm. catalyst zone was less than 0.4°.

The mixture from the reactor was passed through a volumetrically calibrated trap cooled with Dry Ice. Owing to the expense of the hydrocarbons, small runs were employed, ordinarily 1–2 cc. of hydrocarbon. The gas flow-meter data and the rate of hydrocarbon collection provided the necessary data for computing reactant mixture composition and flow rate. The limiting factor in accuracy was the determination of the liquid space velocity of the hydrocarbon. This was subject to an error in many cases as high as 5%.

Analytical Procedures.—Polarimetry: In all cases water-jacketted semi-micro tubes were employed. Since the original rotation of the hydrocarbon was about 6°, values of α/α_0 are subject to an error perhaps reaching 0.5%.

Deuterium content by combustion: To determine hydrogen–deuterium exchange, the hydrocarbon was burned[4] and the density of the recovered water determined by use of a semi-micro float.[5] An accuracy in per cent. of deuterium in total hydrogen of the hydrocarbon of about ± 0.01 percentage unit results.

Mass spectroscopy: These determinations were run on a standard mass spectrometer at conventional ionizing voltages by the Analytical Service Division of the Consolidated Engineering Corporation, Pasadena, California. For the distribution of exchanged species, $C_7H_{15}D$, $C_7H_{14}D_2$, ..., C_7D_{16}, for *n*-heptane and 3-methylhexane, analysis was based upon the parent peaks at mass 100 and up. Intensities were normalized to 100.00 at mass 100. Values for relative intensities in the unexchanged hydrocarbon at masses 101 and 102 (due predominately to molecules containing one and two atoms of C^{13}) were subtracted from the corresponding relative intensities of the exchanged hydrocarbon. The resulting values for masses 101, 102 and up were divided in each case by the sum of the normalized intensities for the exchanged hydrocarbon at 100 and up. The resulting numbers, multiplied by 100, are listed as the percentages of the appropriate species $C_7H_{16-x}D_x$. This computation assumes that all species have the same ionization probability, it ignores possible changes in the sensitivity of the parent peak occasioned by isotopic substitution, and it ignores the contribution of the carbonium ion peak at mass 99. Error from the latter source is small since the intensity at mass 99 is but 2% of that of the parent peak for 3-methylhexane and negligible for *n*-heptane. In terms of the measurement of the original mass spectroscope traces, the percentage of an individual species is subject to an error reaching about 0.05 percentage unit.

Runs 156, 172, 173 and 195 were analyzed at higher sensitivity and higher hydrocarbon pressure than the earlier runs and are probably several-fold more accurate.

Experimental Results

Isomerization and Hydrogenolysis.—To determine whether isomerization or hydrogenolysis accompanies the racemization and exchange reactions to be described, the infrared absorption spectrum of a sample of (+)3-methylhexane which had been 99.6% racemized at 147° was compared with that of the starting material both on the automatic per cent. transmission recording Beckman IR2T and by a substitution method at 20 selected wave lengths on the Beckman IR2. The two spectra were indistinguishable. No more than a few tenths % of isomerization could have occurred. Stepwise hydrogenolysis is excluded to the same extent. Mass spectroscopic examination of the off-gas from an extensive exchange run (run 129) indicated the presence of a few % of light hydrocarbons. At moderate degrees of racemization and exchange, hydrogenolysis and isomerization, if any, are minor reactions.

Racemization of (+)3-Methylhexane.—Racemization occurs at rates convenient for measurement when hydrocarbon and hydrogen are passed over nickel kieselguhr catalysts at 90 to 140°. The dependence of rate upon flow rate, hydrocarbon pressure, hydrogen pressure and temperature has been examined.

Let R be the rate of formation of optically inactive material expressed in cc. per 2 cc. of catalyst per hour. It will be a function of hydrocarbon pressure, hydrogen pressure and temperature if no side reactions occur. It may be evaluated in principle by measurement of racemization at very high values of L (hourly liquid space velocity of hydrocarbon) for, in such case, the decline in rotation of the hydrocarbon as it passes through the catalyst bed can be neglected. The fractional loss in passage through an infinitesimal layer of catalyst, d V, will be

$$-\mathrm{d}\alpha/\alpha = (R/L)(\mathrm{d}V/V_0)$$

where V_0, the total volume of the catalyst, is taken as unity. Upon integrating between the limits of zero and V_0

$$\ln (\alpha_0/\alpha) = R/L \qquad \text{(I)}$$

The hypotheses involved may be tested by testing the constancy of the expression $L \ln (\alpha_0/\alpha)$ where R is held constant by maintaining the temperature and the pressures of hydrogen and hydrocarbon constant. Table I presents such data. With the relatively simple apparatus employed, it was not feasible to duplicate exactly the pressures of hydrogen and hydrocarbon. The values of R have been corrected to the conditions of run 175 according to pressure dependence relations established in subsequent sections. The corrections are small.

TABLE I

EFFECT OF FLOW RATE UPON RACEMIZATION OF (+)3-METHYLHEXANE AT 122°

Run no.	L	p_{3MH}, mm.	p_{H_2}, mm.	α/α_0	R	R (cor.)
174	0.42	130	614	0.831	0.078	0.084
175	1.73	154	590	.918	.148	.148
176	1.30	158	586	.889	.152	.150
177	1.80	151	602	.932	.127	.129
178	0.26	146	607	.678	.101	.104
179	0.86	160	596	.849	.141	.141
180	1.95	159	597	.928	.143	.143
181	0.66	177	579	.793	.153	.144

Values in the last column of Table I are satisfactorily constant save for the values at the lowest two flow rates. Similar results were obtained in four other sequences, each containing three to five runs. Below flow rates of about 0.5, erratic, low results appeared in every such run save one. The origin of this is obscure. It might result from inhibition by traces of by-products or by water vapor very slowly evolved from the catalyst, or from change in flow patterns through the catalyst bed (change in "catalyst efficiency factor").

In runs to be presented, values of total flow rate (hydrogen plus hydrocarbon) seem adequate, in general, to avoid serious complications.

Table II presents the variation of rate with variation in hydrogen pressure when the pressure and space velocity of hydrocarbon are maintained approximately constant at 136 mm. and 0.80. To achieve variation in hydrogen pressure,

TABLE II

DEPENDENCE OF RACEMIZATION UPON HYDROGEN PRESSURE

Run no.	T, °C.	L	p_{3MH}, mm.	p_{H_2}, mm.	p_{He} mm.	α/α_0	R
182	122	0.80	133	608	0	0.866	0.116
183	122	.86	136	323	282	.805	.187
184	122	.82	134	96	511	.622	.390
185	122	.80	134	607	0	.859	.121
186	122	.80	140	0	601	.416	.702
187	121	.80	134	607	0	.802	.178
188	121	.78	135	607	0	.882	.099
189	121	.80	138	0	604	.442	.654
190	121	.78	135	0	607	.649	.337
191	121	.78	134	0	608	.804	.170
192	121	.80	140	0	602	.925	.063

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[4] R. L. Burwell, Jr., and G. S. Gordon, III, THIS JOURNAL, **70**, 3128 (1948).

[5] M. Randall and B. Longtin, *Ind. Eng. Chem., Anal. Ed.*, **11**, 44 (1939).

part of the hydrogen was replaced by helium. Helium is assumed to be without effect.

As shown in the first four runs, the rate of racemization increases with decreasing hydrogen pressure. The rate dependence can be expressed as proportional to $p_{H_2}^{-0.65}$. In a similar series at 125°, a hydrocarbon pressure of 54 mm. and a space velocity of 0.28, the term was $p_{H_2}^{-0.47}$. The determination of the precise kinetics does not lie within the scope of this investigation. It will suffice to say that the hydrogen pressure dependence is about the minus half power in the range studied.

When the hydrogen flow is replaced entirely by helium, the rate at first climbs markedly, as shown in runs 186 and 189, and then steadily sinks. The sequence, runs 185 to 188, shows that after a short period without hydrogen an augmented value of R is found when full hydrogen pressure is restored during one run but that by the next run a normal value of R obtains.

On a similar series employing (+)3-methylheptane[4] at 127° the decline observed upon replacing hydrogen by helium was more rapid and extensive. When hydrogen was then substituted for helium, the thermocouple indicated a catalyst temperature rise of 8°. After restoring hydrogen the activity largely recovered during the course of three runs. (+)3-Methylheptane seems to behave like (+)3-methylhexane although it was not tested in regard to exchange.

The effect of hydrocarbon pressure at constant hydrogen pressure is shown in Table III.

TABLE III

EFFECT OF PRESSURE OF (+)3-METHYLHEXANE UPON RATE OF RACEMIZATION AT 121°

Run no.	L	p_{3MH}, mm.	p_{H_2}, mm.	p_{He}, mm.	α/α_0	R	$R(p_{3MH})^{-1/3}$
143	0.30	61	347	347	0.668	0.121	0.0300
144	.29	59	348	348	.679	.112	.0288
145	.75	149	341	265	.810	.157	.0297
146	.73	138	329	287	.813	.150	.0290
147	.28	57	351	351	.670	.112	.0292
148	.15	30	349	380	.503	.102	.0329
149	.26	55	351	351	.654	.112	.0295
150	.07	15	372	371	.375	.069	.0279

Under these conditions the variation in rate is adequately represented by a term of the form $(p_{3MH})^{1/3}$.

Table IV presents the temperature dependence of the rate of racemization. Hydrocarbon pressures were 175 ± 5 mm., hydrogen pressures, 567 ± 5 mm.

If log R be plotted against $1/T$, the points fall on a straight line to within the precision of the data save for run 169. Ignoring this, the activation energy is 26 kcal. For the exchange reaction between methane and deuterium an activation energy of 28 kcal. has been reported[1a] and for that with propane, roughly 19 kcal.[1c]

TABLE IV

EFFECT OF TEMPERATURE UPON THE RACEMIZATION OF (+)3-METHYLHEXANE

Run no.	T, °K.	L	α/α_0	R
162	415.0	1.15	0.538	0.712
163	392.2	1.15	.882	.143
164	375.9	1.15	.971	.035
165	392.2	1.20	.911	.113
166	404.0	1.25	.772	.322
167	409.8	1.20	.648	.519
168	427.4	1.25	.215	1.920
169	400.0	1.25	.754	0.354

An attempt was made to determine the relative rates of racemization of 3-methylhexane and hydrogenation of an olefin of the same carbon skeleton. A mixture containing 5.2% 3-methyl-2-pentene (from dehydration of 3-methyl-3-pentanol) in 3-methylpentane was employed. This pair was employed since but one *cis–trans* pair of olefins resulted from the dehydration, whereas with 3-methyl-3-hexanol one would have obtained two such pairs. At hydrocarbon pressures of about 145 mm. and space velocities of about 0.38, and at temperatures between 34 and 150°, the infrared spectrum of the condensate was indistinguishable from that of 3-methylpentane. Less than 0.5% olefin could have remained.

It may appear odd that (+)3-methylhexane was prepared by hydrogenating olefin of that structure over the same catalyst as was later employed to racemize it. In fact, however, some racemization was observed in the preparation particularly when the bomb temperature was allowed to exceed 70°. To see if the 120 atmospheres of hydrogen influenced the result, olefin was hydrogenated at 45°, olefin pressure 20 mm., space velocity 0.06 and hydrogen pressure 720 mm. The rotation of the resultant 3-methylhexane was substantially identical with that prepared at high hydrogen pressures.

Effect of Deuterium on Rate of Racemization.—Three sets of runs were made in which hydrogen was replaced by deuterium and then restored. Temperatures and hydrocarbon pressures were: 93°, 54 mm.; 124°, 150 mm.; and 125°, 55 mm. To within the precision and reproducibility of our data, no difference in rate could be detected.

Exchange of Hydrocarbons with Deuterium.—Exchange accompanies the racemization of 3-methylhexane when deuterium is employed as the carrier gas as shown in Table V. Results of the mass spectrographic analysis of the products of some of the runs of Table V are given in Table VI.

TABLE V

EXCHANGE EXPERIMENTS

Run no.	Hydrocarbon[b]	T, °C.	L	p_{HC}, mm.	p_{D_2}, mm.	α/α_0	R	D, %[c]
16	3MH	115	0.75	240	510	0.987	0.010	0.77
17	3MH	128	.90	265	485	.979	.019	1.64
18	3MH	113	.80	260	490	.992	.006	0.34
19	3MH	101	.90	275	475	.992	.007	0.16
23[a]	3MH	100	.68	202	548	.939	.043	3.33
24	3MH	115	.72	222	528	.836	.129	9.95
25	3MH	130	.69	217	533	.527	.442	16.8
27	3MH	115	.63	203	547	.779	.158	11.1
28	3MH	100	.63	205	545	.902	.065	7.13
84[a]	3MH	122	.74	214	536	.765	.198	14.30
85	S	122	.96	233	517	...	...	14.78
86	3MH	122	.90	229	521	.765	.241	11.68
115[a]	S	86	.53	164	586	...	...	2.38
118	33MH	86	.32	122	621	...	...	0.83
119	223MB	86	.46	199	632	...	...	0.15
156[a]	223MB	119	.34	122	534	...	...	1.91
172	3MH	124	1.15	178	566	.885	.140	7.95
173	3MH	103	1.20	183	561	.951	.061	3.38
193	3MH	118	0.72	138	603	.831	.133	11.91
194	S	118	.72	137	604	...	...	13.30
195	3MH	118	.72	135	606	.858	.101	9.57

[a] Different catalyst preparation follows. [b] 3MH is 3-methylhexane, S is heptane, 33MH is 3,3-dimethylhexane and 223MB is 2,2,3-trimethylbutane. [c] Deuterium atom % in hydrocarbon hydrogen by combustion analysis.

In the last two rows of Table VI, the deuterium content computed from the data in the table is compared with that found by combustion. The agreement is good considering that the computation places most weight upon the most exchanged species which are known in many cases to but very low accuracy. In run 18, for example, the listed % of $C_7H_6D_{10}$ and up depends upon mere wiggles in the mass spectrograph trace, definite but of no precision.

At low conversions, if the fraction of molecules exchanged be x, the fraction adsorbed and subjected to exchange twice is $x^2/2$. Thus, at 8% or lower, the contribution of species formed by successive exchanges is negligible.

The catalyst employed in runs 16–19 was much less active than others probably owing to inadequate reduction. The results of the four runs may be taken as equivalent though with decreasing conversion the more exchanged species cannot be detected.

A maximum of seven hydrogen atoms are exchanged in 2,2,3-trimethylbutane (runs 119 and 156). Owing to the minuteness of the parent peak, the analysis was performed at mass 85, *et seq.* These peaks result from the carbonium ion formed by loss of a methyl group attached to the 2-position. It appears unlikely that this could lead to error in the maximum number of hydrogen atoms exchanged or to much error in the relative abundance of the various exchanged species.

TABLE VI

MASS SPECTROGRAPHIC ANALYSES

Hydrocarbon	3MH	3MH	3MH	3MH	3MH	S	33MH	223MB	223MB	3MH	3MH	3MH
Run no.	16	17	18	19	23	115	118[a]	119	156	172	173	195
% Molecules with 1 D	0.58	1.61	0.61	0.33	1.15	0.95	0.51	0.14	2.65	2.39	1.01	2.32
2 D	.34	0.99	.46	.24	0.86	1.10	.34	.26	3.46	1.86	1.00	1.99
3 D	.37	.92	.39	.18	.83	0.70	.36	.11	2.06	1.54	0.83	1.91
4 D	.31	.78	.32	.13	.65	.47	.36	.05	1.24	1.19	.61	1.91
5 D	.32	.68	.31	.16	.55	.39	.41	.04	0.74	1.01	.49	1.92
6 D	.26	.47	.21	.11	.47	.33	.32	..	.42	0.87	.38	1.85
7 D	.16	.34	.15	.05	.42	.27	.27	..	.23	.86	.37	1.70
8 D	.13	.22	.10	.05	.40	.23	.04	..	...	.85	.33	1.46
9 D	.09	.17	.07	.02	.37	.22	..	..	...	.90	.26	1.24
10 D	.07	.15	.05	..	.40	.22	..	..	...	1.03	.29	1.11
11 D	.05	.14	.05	..	.42	.22	..	..	...	1.17	.35	1.05
12 D	.05	.10	.04	..	.46	.22	..	..	...	1.26	.35	1.05
13 D	..	.09	.03	..	.48	.22	..	..	...	1.26	.43	1.06
14 D	..	.06	.02	..	.47	.19	..	..	...	1.05	.48	1.11
15 D	..	..	.03	..	.40	.19	..	..	...	0.64	.53	0.99
16 D	..	..	.02	..	.18	.16	..	..	...	.21	.38	0.59
Total mol. exchanged, %	2.73	6.72	2.86	1.26	8.51	6.08	2.61	0.60	10.80	18.09	8.09	23.26
Total D in hydrocarbon	0.74	1.73	0.77	0.25	3.67	2.19	0.53	.09	1.79	8.14	3.60	10.15
Total D by combustion	0.77	1.64	0.34	0.16	3.33	2.38	0.83	.15	1.81	7.95	3.38	9.57

[a] This computation excludes ethyl group. See text.

The data on 3,3-dimethylhexane are less certain. The results for run 118 in Table VI are computed on the basis of mass numbers 85, *et seq.*, owing to near absence of the parent peak. We assume that this corresponds to the carbonium ion formed from the parent molecule ion which has lost an ethyl group. The relatively large intensity at mass 84 (22% of that of mass 85) which was ignored in the calculation may distort the values of absolute abundance of the various exchanged species but cannot change the maximum number of hydrogen atoms exchanged. Similar analysis of the peak at 99, *et seq.*, the carbonium ion formed by loss of a methyl radical, gives a result which agrees to within the relatively low precision occasioned by the rather low intensity of this peak and in particular shows no species beyond D_7. Similar analysis of the peak at 71, *et seq.* (if this be taken as resulting from the carbonium ion resulting from loss of a propyl group), gives the following results for $\%D_1$, 0.19; D_2, 0.22; D_3, 0.44; D_4, 0.16; D_5, 0.06; D_6 and D_7, less than 0.01; molecules exchanged, 1.06% and deuterium %, 0.16.

The simplest interpretation of these data is that the methyl side chains are negligibly exchanged, that 1.06% of the ethyl and 2.61% of the propyl side chains are exchanged, and that exchange in both ethyl and propyl side chains occurs in a negligible fraction of the molecules (owing to results at mass 99, *et seq.*). It seems best to take the molecules exchanged as the sum, 3.67%, and total deuterium as 0.69% (a value in much better agreement with combustion).

Discussion

At temperatures in the vicinity of 90 to 130°, 3-methylhexane, heptane, 2,2,3-trimethylbutane and 3,3-dimethylhexane undergo isotopic exchange when the hydrocarbon vapor and deuterium are passed over a nickel–kieselguhr catalyst as is shown in Tables V and VI. The exchange reaction is not accompanied by skeletal isomerization or hydrogenolysis of carbon–carbon bonds in significant degree. The relative degrees of exchange at comparable conditions are shown in Table VII.[6]

While these computations are not of high precision, they indicate that species behaving like carbonium ions are not involved since in such case one would expect 3-methylhexane to react at rates very much greater than those of heptane. Rather, the variation in rate is more closely analogous to that of free radical reactions.

TABLE VII

RELATIVE EXCHANGE OF SEVERAL HYDROCARBONS

Hydrocarbon	Relative no. of mol. exchanged	Average no. of D atoms per mol.	D in total H of product, %
S	1.00	6.3	1.00
3MH	0.75	6.5	0.77
33MH	.36	4.1	.21
223MB	.13	2.7	.05

Figure 1 presents the estimated % of each exchanged species for various hydrocarbons under the same conditions.[7]

As has been shown, the multiply exchanged species cannot arise from single atom interchanges occurring consequent to repeated successive adsorptions. Thus, the exchange process cannot be ascribed to mere dissociative adsorption to a hydrogen atom and an alkyl fragment followed by combination and evaporation of the alkyl fragment with a deuterium atom, although such dissociative adsorption might be the first step. Rather, once the alkane molecule has been adsorbed, it has a high probability of undergoing reactions leading to extensive exchange before it evaporates.

In the case of heptane and 3-methylhexane all exchanged species from $C_7H_{15}D$ to C_7D_{16} are present. For 3,3-dimethylhexane and 2,2,3-trimethylbutane substantially no exchange is observed beyond seven hydrogen atoms. In 3,3-dimethylhexane a very small peak is observed at eight hydrogen atoms

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(6) In constructing this table, % D by combustion is employed. Run 115 for heptane is taken as standard. Run 118 is employed for 3,3-dimethylhexane. For 2,2,3-trimethylbutane, relative exchange (% D) is taken from run 115, the average number of D atoms per molecule, from run 156. Values are corrected to flow rates of run 115. Relative exchange of heptane and 3-methylhexane is taken by comparison of runs 84, 85 and 86 and 193, 194 and 195; average number of D atoms per molecule is the average of runs 23 and 173. It is assumed that the relative distribution patterns for abundance of exchanged species are constant. This can hardly be rigorously correct.

(7) Run 115 is plotted directly. Run 118 is corrected for flow rate. Run 156 is plotted, multiplied by a scale factor, to reduce the % D to that of run 119 corrected for flow rate. Run 23 is plotted, multiplied by a scale factor to give % D as listed in Table VII. Relative distribution patterns for exchanged species are assumed constant.

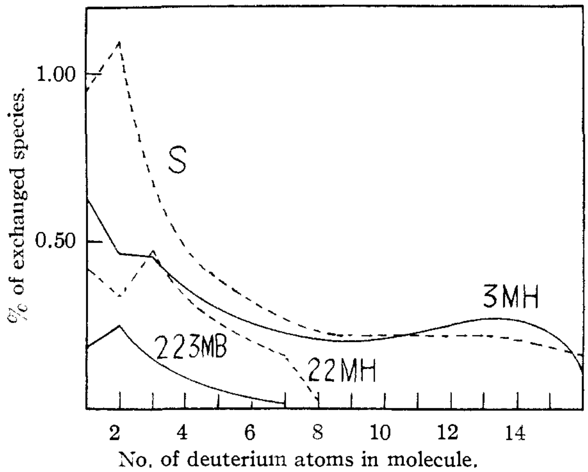

Fig. 1.—Estimated exchange distribution pattern under same operating conditions.

exchanged. However, one-half of this must be expected from $C^{12}{}_7C^{13}H_{11}D_7$.

The number of hydrogen atoms in the propyl and *i*-propyl side-chains of the last two alkanes is seven. It is hard to avoid the conclusion that the process which follows initial adsorption and which leads to multiple exchange cannot propagate past a quaternary carbon atom. This may be related to the difficulty of hydrogenolysis of a carbon–carbon bond on the nickel–kieselguhr catalyst at 200° when one of the carbon atoms has three additional alkyl groups attached to it.[8] On the other hand, as shown by 3-methylhexane, exchange can proceed past a tertiary carbon atom.

The catalyst probably contains a rather large exchangeable hydrogen reservoir.[1c] However, the flushing with deuterium before an exchange run and the relatively large quantities of reactants passed over the catalyst make it unlikely that protium from the exchangeable reservoir seriously affects the distribution pattern. Furthermore, no significant change in the exchange distribution pattern was noticed in successive runs with deuterium. Problems of this nature should be much less important in flow than in static experiments.

Cases of multiple exchange resembling the present work have recently appeared. On evaporated nickel films at about 230°, two processes occur,[9] one forming CH_3D and another CD_4.

On a Fischer–Tropsch catalyst (cobalt, thoria, magnesia, kieselguhr) at 183°, only completely or nearly completely exchanged species appear as primary products in the case of butane and *i*-butane.[10]

At −78°, hydrogenation with deuterium of *cis*-2-butene on a nickel catalyst[11] gives species of other deuterium content than $C_4H_8D_2$ although isobutylene gives 95% $C_4H_8D_2$.

Racemization.—Upon passing a mixture of hydrogen and 3-methylhexane over nickel–kieselguhr at about 120°, a specific racemization of the alkane occurs. It is negligibly accompanied by side reactions. Such pure racemization seems previously unreported as a heterogeneous catalytic process, though the racemization of 3-methylhexane at −80° by chlorosulfonic acid[2] approaches it in selectivity. The process must be closely related, however, to the conversion of the *cis*-dimethylcyclohexanes to the *trans*-compounds over nickel at 170° as reported by Zelinsky and Margolis.[12] The present work emphasizes the danger of stereochemical interconversions in the presence of nickel catalysts at higher temperatures.

The rate data expressing the value of $R = L \ln(\alpha/\alpha_0)$, equation 1, may be reproduced by the equation

$$R = k_0 e^{-26,000/1.987T} p_{H_2}{}^{-n} p_{3MH}{}^{1/3}$$

where n lies between $^1/_2$ and $^2/_3$. Of course, terms of the form, $ap/(1 + ap)$ could equally well represent these data. In the absence of hydrogen the catalyst becomes poisoned, presumably by decomposition of the alkane to carbon and hydrogen or methane.[1] Catalyst activity is slowly restored by treatment with hydrogen at the same temperature, completely at 300°.

Furthermore, the rate of racemization is the same to within experimental uncertainty (±20%) in the presence of deuterium. It is, thus, unlikely that the rate-determining step can involve the participation of hydrogen or deuterium atoms adsorbed on the surface. In particular, if the rate-determining step is that of adsorption (which must equal that of desorption in the steady state) the participation of adsorbed hydrogen atoms in this step is improbable. The breaking of a carbon–hydrogen bond to give initially adsorbed hydrogen atoms and alkyl radicals would, however, be consistent with this result.

We assume that the racemization reaction occurs consequent to the processes leading to isotopic exchange although this cannot be rigorously proved. The kinetics of the exchange reaction have not been investigated, but presumably resemble those of racemization since the degree of exchange, in general, parallels that of racemization in the cases reported here. For propane, Taylor, *et al.*,[1c] reported the rate of the exchange process to be proportional to $p_{D_2}{}^{-0.76} p_{HC}{}^{0.62}$. This resembles the kinetics for racemization (equation (2)).

The relative abundance of exchanged species on the inactive catalyst of runs 16–19, a nearly exponential decline with increasing exchange, suggests that the exchange occurs one atom at a time and that at the end of each such exchange, the alkane has fixed probabilities of either exchanging again or of desorbing.

At low levels of exchange, the exchange pattern of 3-methylhexane on the normal catalyst shows a maximum after an initial decline (runs 23 and 173, Table VI). At greater degrees of exchange, the greater HD content of the hydrogen and also readsorption and exchange must bring the pattern closer to statistical distribution. In run 195, though not run 172, this has so progressed as just about to eliminate the maximum.

As in the case of methane–deuterium exchange,[9]

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[8] V. Haensel and V. N. Ipatieff, THIS JOURNAL, **68**, 345 (1946).

[9] C. Kemball, *Proc. Roy. Soc.* (*London*), **A207**, 539 (1951).

[10] S. O. Thompson, J. Turkevich and A. P. Irsa, THIS JOURNAL, **73**, 5213 (1951).

[11] C. D. Wagner, J. N. Wilson, J. W. Otvos and D. P. Stevenson, *J. Chem. Phys.*, **20**, 338 (1952).

[12] N. D. Zelinsky and E. I. Margolis, *Ber.*, **65**, 1613 (1932).

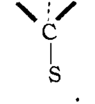
it does not appear possible to accommodate the exchange distribution pattern with one exchange process. Furthermore, the following considerations may affect the pattern. The hydrogen atoms which dissociate from the alkane may not come to equilibrium with the bulk of the adsorbed deuterium atoms before recombination occurs. Thus, the observed extent of exchange would be less than that corresponding to the number of hydrogen atoms which actually dissociate from the alkane.

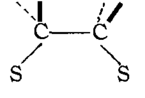
The ratio of the numbers of molecules exchanged to that racemized is given by the ratio of $-\ln Z$ to $-\ln(\alpha/\alpha_0)$ where Z is the fraction of molecules having suffered no exchange. For runs 23, 172, 173 and 195 the ratio is 1.4, 1.6, 1.6 and 1.7, or an average of 1.6. The excess of molecules exchanged may be associated with a process involving exponential decline. In this, molecules initially adsorbed on the propyl or ethyl side chains would largely desorb before exchange propagates to the optically active center. As may be seen in Fig. 1, an adequate number of molecules exchanged but a few times is available to account for this excess.

Partial reversal of the process involved in the hydrogenation of olefins coupled with the double bond isomerization which is known to occur on nickel catalysts and which is accompanied by exchange in the presence of deuterium,[13] provides an attractive possibility for explaining exchange. Indeed, it is difficult to envisage processes of alkane exchange and olefin hydrogenation which do not include some common steps. For example, a dissociatively adsorbed alkane molecule in the Taylor formulation of exchange[1] is identical with the Polanyi half-hydrogenated stage in olefin hydrogenation.

A number of possible mechanisms of this nature exist. The requirement that racemization accompany exchange and that the rate be nearly the same in the presence of either hydrogen or deuterium places drastic limitation on such processes and eliminates many conceivable mechanisms.

Accordingly as one assumes that the terminal stage of hydrogenation involves the addition of one atom of hydrogen or two atoms (or a molecule) of hydrogen, the initial process in racemization and exchange involves the adsorption of alkane as an alkyl radical and a hydrogen atom or as something like adsorbed olefin and two hydrogen atoms. Even if these processes occur at the optically active center, they cannot, *per se*, lead to racemization if the adsorption process proceeds as a stereospecific process. Adsorbed methylethylpropylmethyl radicals are asymmetric as is the analogous adsorbed "olefin."



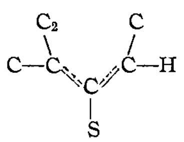


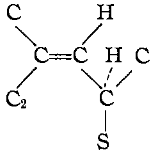
By microscopic reversibility, an alkane of the original configuration would be regenerated on desorption. Similar considerations apply to any double bond migration process in which carbon atom 3 becomes attached to the surface by dissociation of the carbon–hydrogen bond. For example, double bond migration *via* the associative mechanism of olefin hydrogenation would not lead to racemization.

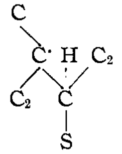
If dissociative adsorption of 3-methylhexane takes place by two processes, one involving retention and one inversion of configuration, then desorption will lead to a partially racemized alkane. If the rates of the two processes are equal, desorption will lead to a completely racemized product; as one rate exceeds the other, a product of less and less racemization results.

Farkas[14] has suggested that mere dissociative adsorption of an optically active hydrocarbon would cause racemization. This could occur, however, only if two stereochemically opposite processes were involved. In the present case, one would have to assume that the two processes occur at nearly equal rates since the rate of adsorption (as measured by the number of molecules which suffer exchange) exceeds that of racemization by but 60%. It does not appear too attractive.

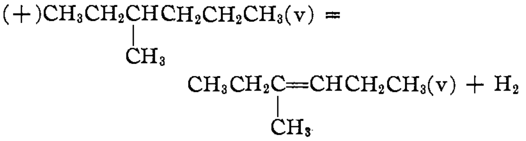
We consider that the mechanism most probably involves a symmetric, adsorbed intermediate, such as an allylic free radical,[13,15] or a non-adsorbed double bond. Such species are







These species, particularly the first and second, are of potential interest as permitting migration of the point of attachment of the hydrocarbon molecule with accompanying isotope exchange. They would not permit exchange to be propagated past a quaternary carbon atom. If one assumes, as would be likely, that such species can be derived from the adsorption of either olefins or alkane, one must assume that the relative probability of migration to hydrogenation (desorption) varies with conditions since we have found that optically active 4-methyl-2-hexene may be hydrogenated over nickel–kieselguhr catalysts at 45° with negligible racemization. Establishment of equilibrium in the vapor phase in the reaction



$$(+)\mathrm{CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2CH_3(v)} = \mathrm{CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CHCH_2CH_3(v)} + \mathrm{H_2} \quad (3)$$

would lead both to racemization and exchange and would avoid the necessity of postulating symmetric adsorbed species. The rate of the reverse reaction is undoubtedly very rapid. We were unable to detect residual olefin when hydrogen and 3-methylpentane containing 5.2% of 3-methyl-2-pentene was passed over the catalyst at temperatures as low as 34°. However, since the equilibrium pressure of olefin at 120° under our condi-

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(13) T. I. Taylor and V. H. Dibeler, *J. Phys. Colloid Chem.*, **55**, 1036 (1951). A detailed presentation of previous work and proposed mechanisms in the field of olefin–hydrogen reactions occurs in this paper. Reference is made to it for citations of the original literature.

(14) A. Farkas, *Trans. Faraday Soc.*, **35**, 906 (1939).

(15) W. Jost, *ibid.*, **35**, 940 (1939).

tions is about 10^{-9} atmosphere, the rate constant of the reverse reaction would have to be enormous. While the process of equation (3) cannot be excluded, it seems unlikely. In any case it could not proceed by the reverse of Beeck's mechanism for olefin hydrogenation.[16] In this a molecule of alkane striking the catalyst would lose two hydrogen atoms and rebound as olefin. The racemized alkane would then contain two and only two deuterium atoms contrary to our experimental results.

The results on nickel–kieselguhr catalysts should not at present be extrapolated to other catalysts. Preliminary experiments in this Laboratory indicate different behavior for cracking catalysts and chromium oxide–alumina catalysts.

Thermomagnetic analysis[17] shows that the ferromagnetism of nickel–kieselguhr as supplied is nearly tripled upon reduction. The ferromagnetism of both forms declines steadily with temperature and reaches low values by 360°. The absence of a Curie point at 357° indicates the absence of any substantial amount of pure, bulk, metallic nickel, but suggests, rather, the presence of a heterogeneous system.

de Lange and Visser[18] report that unreduced nickel–kieselguhr catalysts (20% nickel) possess a layer lattice and that, upon reduction, no X-ray lines characteristic of bulk metallic nickel appear.

It appears desirable to extend these studies to other catalysts known to activate hydrocarbon molecules and particularly to other types of nickel catalysts.

Acknowledgment.—The authors are indebted to the Office of Naval Research which supported this research, to Mr. Frank E. DeBoer who ran the thermomagnetic analysis of the catalyst, to Professor P. W. Selwood, with whom this analysis was discussed, to Dr. Kenneth W. Greenlee of the American Petroleum Institute Project 45 at The Ohio State University for the sample of 3,3-dimethylhexane and to Dr. Paul Cramer of the General Motors Corporation for the 2,2,3-trimethylbutane.

EVANSTON, ILLINOIS

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[16] O. Beeck, *Rev. Modern Phys.*, **17**, 68 (1945).

[17] P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, Chapter VIII.

[18] J. J. de Lange and G. H. Visser, *De Ingenieur*, **58**, O.25 (1946). In connection with this catalyst, see also J. J. B. Van Eijk van Voorthuijsen and P. Franzen, *Rec. trav. chim.*, **70**, 793 (1951), and G. C. A. Schuit and N. H. de Boer, *Nature*, **168**, 1040 (1951).

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY OF MICHIGAN STATE COLLEGE]

The Synthesis of Some Tertiary Amine Derivatives of Mixed Phenyl Alkyl Sulfides

BY MOON HWI KIM[1] AND ROBERT D. SCHUETZ

RECEIVED FEBRUARY 12, 1952

The properties and syntheses of a series of hydrochlorides of tertiary amine derivatives of mixed phenyl alkyl sulfides, ω-(N,N-disubstituted amino)-alkylphenyl sulfides, are described.

As part of a study of sulfur-containing compounds of pharmacological interest, some tertiary amine derivatives of mixed phenyl alkyl sulfides, $C_6H_5S(CH_2)_nNR_2$ (I), were prepared because of the interesting activity possessed by the corresponding ether analogs.

In one of the two reported cases of an investigation of the physiological action of compounds of this type Buchel and Tchoubar[2] compared β-diethylaminoethylphenyl sulfide and β-diethylaminoethyl *o*-tolyl sulfide with their corresponding oxygen ethers. In the other investigation Kohler[3] reported a comparison of the physiological actions of β-ethylaminoethylphenyl sulfide and β-ethylaminoethyl *o*-tolyl sulfide with β-dimethylaminoethylphenyl ether and bis-(β-*o*-toloxyethyl)-methylamine. However, in neither of these limited investigations were a sufficient number of sulfur compounds prepared to allow a complete physiological study to be made of them.

The aminoalkyl phenyl sulfides of the present investigation were prepared by the following sequence of reactions

$$C_6H_5SH + Cl(CH_2)_nOH \xrightarrow{NaOH} C_6H_5S(CH_2)_nOH \quad (II)$$

$$\xrightarrow[C_5H_5N]{SOCl_2} C_6H_5S(CH_2)_nCl \ (III) \xrightarrow[C_6H_5CH_3]{R_2NH} (I)$$

The ω-hydroxyalkylphenyl sulfides (II) with two to six carbon atoms in the alkyl chain, including a branched alkyl chain of three carbon atoms, were prepared by the interaction of thiophenol and the corresponding chlorohydrin, extending the procedure developed by Kirner and Richter[4] for the preparation of β-hydroxyethyl and γ-hydroxypropylphenyl sulfides.

The ω-hydroxylalkylphenyl sulfides were further characterized by the preparation of the 3,5-dinitrobenzoate and *p*-nitrobenzoate derivatives. The properties of those derivatives which have not previously been reported are listed in Table II.

The ω-chloroalkylphenyl sulfides (III) were obtained from the corresponding ω-hydroxyalkylphenyl sulfides by a modification of the method of Darzens.[5]

In an effort to shorten the synthetic scheme shown above, by preparing the ω-chloroalkylphenyl sulfides directly from thiophenol, the use of ω-

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[1] Abstracted in part from the M.S. thesis, Michigan State College, of M. H. Kim, 1950.

[2] M. L. Buchel and B. Tchoubar, *Compt. rend. soc. biol.*, **141**, 34 (1947).

[3] D. Kohler, *ibid.*, **141**, 233 (1947).

[4] W. R. Kirner and G. H. Richter, THIS JOURNAL, **51**, 3409 (1929).

[5] G. Darzens, *Compt. rend.*, **152**, 1314 (1911).