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Isomerization of Saturated Hydrocarbons. XV.[1] The Hydro-isomerization of Ethyl-α-C^{14}-cyclohexane and Ethyl-β-C^{14}-cyclohexane

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Ethyl-α-C^{14}-cyclohexane and ethyl-β-C^{14}-cyclohexane were synthesized and subjected to a hydro-isomerization reaction. The reaction was performed in a flow type apparatus in the presence of a nickel–silica–alumina catalyst at 360° and under 25 atmospheres pressure. The radioactive cyclohexanes yielded a mixture of alkylcyclohexane and alkylcyclopentane isomers. The relative concentrations of 1,2-, 1,3- and 1,4-dimethylcyclohexanes were found to be nearly equal to their thermodynamic equilibrium concentrations. A new species of ethylcyclohexane was produced during the reaction in an amount almost corresponding to its equilibrium concentration. A near statistical distribution of the radioactivity between the ring and side chain of 1,2-, 1,3- and 1,4-dimethylcyclohexanes was found, which indicates that a deep seated skeletal rearrangement occurred which must have involved repeated ring contraction and expansion. A carbonium ion mechanism explains the almost complete scrambling of the carbon atoms in the alkylcyclohexanes.

It has been reported[3] previously that ethylcyclohexane undergoes hydro-isomerization in the presence of nickel–silica–alumina catalyst to yield a product consisting principally of 1,2- and 1,1-dimethylcyclohexane and 1,2,3- and 1,1,2-trimethylcyclopentane. However, Pitts, Connor and Leum[4] have recently reported that the two-stage isomerization of ethylbenzene in the presence of platinum on deactivated silica–alumina catalyst yielded a mixture containing all of the xylene isomers. These latter authors suggest that ethylbenzene was first hydrogenated to ethylcyclohexane which underwent isomerization to dimethylcyclohexanes which in turn were dehydrogenated to yield the corresponding aromatics.

At least two paths exist by which an alkylcyclohexane, with a side chain larger than methyl, could be converted into polymethylated cyclohexanes. The side chain only could be involved and the ring remain intact during the rearrangement.[3,5] On the other hand, the ring could undergo a series of contractions and expansions by means of which the original side chain would become part of the ring and part of the original ring would become part of the side chain.[6-8] Justification for the latter suggestion can be had from studies of five six-membered ring interconversions which have shown that these two ring sizes are in dynamic equilibrium in the presence of an isomerization catalyst.[1,9]

It seemed of interest therefore to investigate the nickel–silica–alumina catalyzed hydro-isomerization of ethylcyclohexane using ethyl-α-C^{14}-cyclohexane and ethyl-β-C^{14}-cyclohexane. The radioactivity distribution between the ring and side chain of the dimethylcyclohexanes produced would permit a more complete understanding of the mechanism of the rearrangement.

Results and Discussion

Ethyl-α-C^{14}-cyclohexane and ethyl-β-C^{14}-cyclohexane were synthesized and subjected to the hydro-isomerization reaction in the presence of nickel–silica–alumina catalyst at 360°, 25 atmospheres pressure and a molar hydrogen-to-hydrocarbon ratio of 4:1. Two experiments were performed using ethyl-α-C^{14}-cyclohexane at an hourly liquid space velocity of 1.0. Two experiments were performed using ethyl-β-C^{14}-cyclohexane, one at an hourly liquid space velocity of 1.0 and the other at an hourly liquid space velocity of 3.0.

The method employed for analysis of the hydro-isomerate is illustrated in Diagram 1. Radioactivity determinations were made on the enclosed compounds. The non-geminal alkylcyclohexanes were selectively dehydrogenated to the corresponding aromatic hydrocarbons under conditions where 1,1-dimethylcyclohexane was not dehydrogenated. The aromatic hydrocarbons were oxidized to the corresponding aromatic acids, which were isolated, purified and assayed. By use of the isotope dilution technique,[10] the conversion and composition of the alkylcyclohexanes were determined. The aromatic acids obtained were degraded in order to

TABLE I

THE COMPOSITION OF THE ALKYLCYCLOHEXANES IN THE HYDRO-ISOMERATE OBTAINED FROM ETHYL-α-C^{14}-CYCLOHEXANE AND ETHYL-β-C^{14}-CYCLOHEXANE[a]

Catalyst: nickel–silica–alumina, temp. 360°, pressure 25 atm., molar ratio of hydrogen/hydrocarbon = 4.0

Experiment	2	3	4	5
Ethyl-x-C^{14}-cyclohexane, x =	α		β	
H.L.S.V.[b]	1.0	1.0	1.0	3.0
Conversion, %	43.4	43.6	45.0	30.5
Composition of hydro-isomerate, wt. %				
Ethylcyclohexane[c]	56.6	56.4	55.0	69.5
Ethylcyclohexane[d]	3.3	3.6	3.2	2.4
1,2-Dimethylcyclohexane	5.2	4.4	3.8	2.9
1,3-Dimethylcyclohexane	13.2	11.8	10.5	7.9
1,4-Dimethylcyclohexane	7.0	6.8	6.6	4.7

[a] Determined by the isotope dilution technique. [b] Hourly liquid space velocity or volume of liquid per volume of catalyst per hour. [c] Recovered unreacted ethylcyclohexane. [d] Recovered reacted ethylcyclohexane.

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[1] For paper XIV of this series see H. Pines and R. W. Myerholtz, Jr., THIS JOURNAL, **77**, 5392 (1955).

[2] Universal Oil Products Predoctoral Fellow 1953–1956.

[3] F. G. Ciapetta, *Ind. Eng. Chem.*, **45**, 159 (1953).

[4] P. M. Pitts, Jr., J. E. Connor, Jr., and L. N. Leum, *ibid.*, **47**, 770 (1955).

[5] R. C. Hansford in "Physical Chemistry of the Hydrocarbons," Vol. II, Academic Press, Inc., New York, N. Y., 1953, p. 290.

[6] H. Pines and J. M. Mavity in "The Chemistry of Petroleum Hydrocarbons," Vol. III, Reinhold Publishing Corporation, New York, N. Y., 1955, p. 9.

[7] H. Pines, R. C. Olberg and V. N. Ipatieff, THIS JOURNAL, **74**, 4872 (1952).

[8] G. R. Donaldson, L. F. Pasik and V. Haensel, *Ind. Eng. Chem.*, **47**, 731 (1955).

[9] R. Van Volkenburgh and K. W. Greenlee, Abstract of Paper, 118th Meeting, A.C.S., Chicago, Ill., Sept. 3–9, 1950, p. 36.

[10] F. A. Paneth, "Radioelements as Indicators," McGraw-Hill Book Co., Inc., New York, N. Y., 1928.

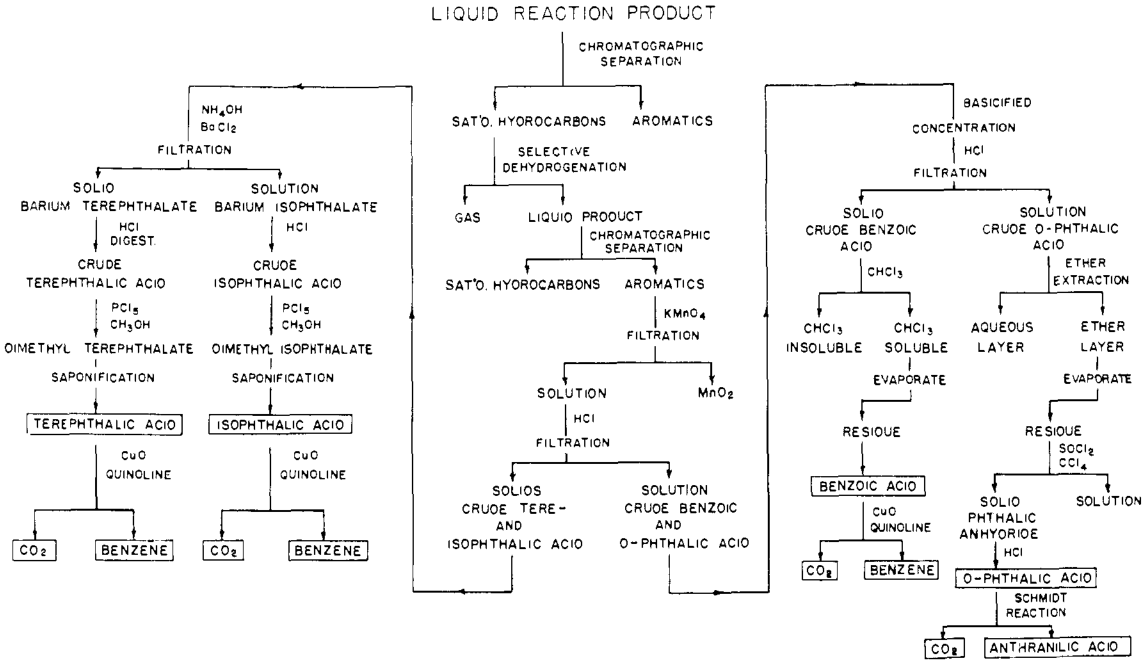

Diagram 1.—Procedure used for the analysis of hydro-isomerate (radioactivity determinations were made on the enclosed compounds.)

determine the isotopic distribution between the ring and the side chain.

The composition of the alkylcyclohexanes in the product obtained from the hydro-isomerization of ethyl-α- and β-C^{14}-cyclohexane is given in Table I. The product distribution was calculated from dilution data which are summarized in Tables II and III. The relative concentrations of the various alkylcyclohexanes in the reaction products were found to approach their thermodynamic equilibrium concentrations, Table IV.

It is significant that ethylcyclohexane which underwent reaction is also approaching its thermodynamic equilibrium value. The concentration of the recovered reacted ethylcyclohexane was calculated on the basis of its isotopic distribution between ring and side chain. This calculation is explained in the Experimental section.

The results show that ethylcyclohexane, upon contact with the nickel–silica–alumina catalyst, underwent a rapid and reversible isomerization to its dimethylcyclohexane isomers.

It was observed that only about 85% of the product underwent dehydrogenation to the corresponding aromatic hydrocarbons. The remaining 15% was composed, according to the index of refraction, of alkylcyclopentanes and of 1,1-dimethylcyclohexane. If it is assumed that the latter is also present in amounts corresponding to its equilibrium concentration, namely, about 7%, relative to the other alkylcyclohexanes produced, it can then be concluded that the ratio of alkylcyclohexanes to alkylcyclopentanes produced was also approaching an equilibrium composition.[11]

The radioactivity distribution between the ring and side chain in alkylcyclohexanes obtained from the hydroisomerization of ethylcyclohexanes is summarized in Table V. This summary is based on the radiochemical assay data obtained from the degradation experiments of the corresponding aromatic acids; Tables VI and VII.

The radioactivity distribution data show that an extensive rearrangement of the carbon skeleton of the alkylcyclohexanes took place during the hydroisomerization reaction in the presence of nickel–silica–alumina catalyst. The approach to statistical distribution (statistical distribution, ring, 75%; side chain, 25%) of the isotope between ring and side chain in the alkylcyclohexanes obtained from the hydro-isomerization of ethyl-α-C^{14}-cyclohexane at H.L.S.V. of 1.0 is very close (Table V). In the case of the dimethylcyclohexanes derived from ethyl-β-C^{14}-cyclohexane, the radioactivity distribution, although not statistical, is still very extensive. At the higher space velocity, less radioactivity enters the ring than at the lower space velocity (Table V).

A similar scrambling of the carbon atoms was observed when propane-1-C^{13} and *n*-butane-1-C^{13} were contacted in the presence of aluminum bromide promoted with water.[12,13] In the study, however, of the liquid phase isomerization of 2-methylbutane-1-C^{14} over an aluminum bromide catalyst[14] and in the case of the isomerization of *t*-butyl- and *t*-amyl chloride[15] such a deep seated scrambling of the carbon atoms was not found. Similarly, in the carbonium ion type reactions of 2,3,3-trimethyl-2-

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(11) J. E. Kilpatrick, H. G. Werner, C. W. Beckett, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **39**, 523 (1947).

(12) O. Beeck, J. W. Otvos, D. P. Stevenson and C. D. Wagner, *J. Chem. Phys.*, **16**, 255 (1948).

(13) J. W. Otvos, D. P. Stevenson, C. D. Wagner and O. Beeck, *ibid.*, **16**, 745 (1948).

(14) J. D. Roberts and G. R. Coraor, THIS JOURNAL, **74**, 3586 (1952).

(15) J. D. Roberts, R. E. McMahon and J. S. Hine, *ibid.*, **72**, 4237 (1950).

TABLE II

RADIOCHEMICAL ASSAY AND DILUTION DATA FOR THE HYDRO-ISOMERIZATION OF ETHYL-α- AND β-C^{14}-CYCLOHEXANE

Experiment[i]	1[a] (Blank)	2	3	4	5
Wt. hydro-isomerate, g.	2.5030[b]	5.6440	5.7544	5.8807	10.8030
Init. specific activ.[c]	52388	8323	16590	31136	106904
	(7 × 7484)	(7 × 1189)	(7 × 2370)	(8 × 3892)	(8 × 13363)
Carrier cyclohexane and wt., g.[d]					
1,2-Dimethyl-	0.8769[e]	0.7760	1.5505	1.5604	1.5635
1,3-Dimethyl-	.8650[e]	.7599	1.5301	1.5347	1.5301
1,4-Dimethyl-	.8612[e]	.7633	1.5321	0.7989	1.5276
Aromatic acid and specific activ.[c]					
o-Phthalic	28[f]	2296[f]	2338[f]	3885	17856
	(14 × 2)	(14 × 164)	(14 × 167)	(8 × 485)	(8 × 2232)
Isophthalic	40[g]	4120[g]	5110[g]	8944	38120
	(10 × 4)	(10 × 412)	(10 × 511)	(8 × 1118)	(8 × 4765)
Terephthalic	256	2830[h]	3390[h]	10150[h]	26490[h]
	(8 × 32)	(10 × 283)	(10 × 339)	(10 × 1015)	(10 × 2649)

[a] The ethyl-α-C^{14}-cyclohexane was not contacted with the nickel–silica–alumina catalyst. [b] Aromatic hydrocarbons from the dehydrogenation of ethyl-α-C^{14}-cyclohexane. [c] See end of Experimental for the definition of this value. [d] These hydrocarbons were added to the hydro-isomerate. [e] Added as the corresponding xylene. [f] Determined by combustion of phthalanil. [g] Determined by combustion of dimethyl isophthalate. [h] Determined by combustion of dimethyl terephthalate. [i] Experiments 1–3 were made with α- and experiments 4–5 with β-ethyl-C^{14}-cyclohexane.

TABLE III

RADIOCHEMICAL ASSAY AND DILUTION DATA FOR THE CONVERSION OF ETHYL-α-C^{14}-CYCLOHEXANE AND ETHYL-β-C^{14}-CYCLOHEXANE

Experiment	2	3	4	5
Wt. of hydro-isomerate, g.	5.5583	1.3718	0.7754	0.7714
Initial specific activity[a]	2667	16590	31136	106904
	(7 × 381)	(7 × 2370)	(8 × 3892)	(8 × 13363)
Wt. of carrier ethylcyclohexane, g.[b]	3.1292	4.1613	5.4639	6.9991
Aromatic acid and specific activity[a]	1372	2737	..	..
Benzoic	(7 × 196)	(7 × 391)	2376	7863
p-Ethylbenzoylpropionic acid	..	..	(12 × 198)	(12 × 653)

[a] See end of the Experimental section for the definition of this value. [b] This hydrocarbon was added to the hydro-isomerate.

TABLE IV

COMPARISON OF EXPERIMENTAL AND THEORETICAL THERMODYNAMIC EQUILIBRIUM CONCENTRATIONS OF THE ALKYLCYCLOHEXANES AT 360°

Experiment Compound	2	3	4	5	Calcd.[a]
Ethylcyclohexane	11.5	13.5	13.3	13.4	12.1
1,2-Dimethylcyclohexane	18.1	16.5	15.8	16.2	19.8
1,3-Dimethylcyclohexane	46.0	44.4	43.6	44.2	45.1
1,4-Dimethylcyclohexane	24.4	25.6	27.3	26.2	23.1

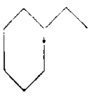
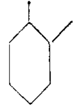
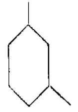
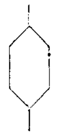
[a] Taken from the data of Kilpatrick, Werner, Beckett, Pitzer and Rossini[11] and converted to a 1,1-dimethylcyclohexane free basis.

butanol-1-C^{14} it was found in the presence of concentrated hydrochloric acid and zinc chloride that the carbon-14 isotope was distributed essentially equally among the five methyl groups rather than being distributed throughout the whole molecule.[16]

When the concentrations of the corresponding cycloalkanes present in the hydro-isomerate of experiment 4 (Table I) are compared with the concentrations of the xylenes, it is apparent that more *o*-xylene is present than would be expected if the corresponding cycloalkanes were dehydrogenated at equal rates. However, this point was not investigated further. The radioactivity distribution in *p*-xylene was comparable to that obtained for 1,4-dimethylcyclohexane (Table VIII).

TABLE V

THE RADIOACTIVITY DISTRIBUTION BETWEEN THE RING AND SIDE CHAIN OF THE ALKYLCYCLOHEXANES FROM THE HYDRO-ISOMERIZATION OF ETHYL-α- AND β-C^{14}-CYCLOHEXANE

		Compound			
Expt.	% of the total radioactivity[a]				
2	Ring	4		77	66
	Side chain	96[c]		20	23
	Difference[b]	..		−3	−11
3	Ring	5	81[c]	77	80
	Side chain	95[c]	19	21	21
	Difference[b]	..	..	−2	+1
4	Ring	3	62[c]	58	60
	Side chain	97[c]	38	41	41
	Difference[b]	..	..	−1	+1
5	Ring	2	54[c]	52	53
	Side chain	98[c]	46	48	49
	Difference[b]	..	..	0	+2

[a] Numbers are rounded off to the nearest whole number. [b] Difference between recovered radioactivity and 100% recovery. [c] Determined by difference.

Mechanism of the Reaction.—Contrary to the previously discussed work of Ciapetta,[3] it has been found in the present investigation that the nickel–silica–alumina catalyst isomerized ethylcyclohex-

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(16) J. D. Roberts and J. A. Yancey, THIS JOURNAL, 77, 5558 (1955).

TABLE VI

RADIOCHEMICAL ASSAY DATA

THE DECARBOXYLATION OF THE AROMATIC ACIDS DERIVED FROM THE ALKYLCYCLOHEXANES PRODUCED BY THE HYDRO-ISOMERIZATION OF ETHYL-α- AND β-C^{14}-CYCLOHEXANE

		Specific activity[a]		
		Benzoic acid	Isophthalic acid	Terephthalic acid
Expt. 1[b]	Acid	8568 (7 × 1224)	. .	. .
	Benzene	18 (6 × 3)	. .	. .
	Carbon dioxide	[c]	. .	. .
Expt. 2	Acid	8729 (7 × 1247)	1648 (8 × 206)	2144 (8 × 268)
	Benzene	354 (6 × 59)	1272 (6 × 212)	1404 (6 × 234)
	Carbon dioxide	[c]	336 (2 × 168)	498 (2 × 249)
Expt. 3	Acid	10262 (7 × 1466)	7296 (8 × 912)	6184 (8 × 773)
	Benzene	462 (6 × 77)	5640 (6 × 940)	4926 (6 × 821)
	Carbon dioxide	[c]	1536 (2 × 768)	1316 (2 × 658)
Expt. 4	Acid	2541 (7 × 363)	15304 (8 × 1913)	8976 (8 × 1122)
	Benzene	1806 (6 × 301)	8922 (6 × 1487)	5382 (6 × 897)
	Carbon dioxide	707 (1 × 707)	6276 (2 × 3138)	3710 (2 × 1855)
Expt. 5	Acid	2751 (7 × 393)	6728 (8 × 841)	5920 (8 × 740)
	Benzene	1782 (6 × 297)	3486 (6 × 581)	3156 (6 × 526)
	Carbon dioxide	933 (1 × 933)	3222 (2 × 1611)	2888 (2 × 1444)

[a] See end of the Experimental section for the definition of this value. [b] The ethyl-α-C^{14}-cyclohexane was not contacted with the nickel–silica–alumina catalyst. [c] The radioactivity of the carbon dioxide was too high to be comparable with the other values.

TABLE VII

RADIOCHEMICAL ASSAY DATA

RESULTS OF THE SCHMIDT REACTION ON *o*-PHTHALIC ACID

	Specific activity[a]		
	o-Phthalic acid	Carbon dioxide	Anthranilic acid
Expt. 3	2400 (8 × 300)	226 (1 × 226)	[b]
Expt. 4	8872 (8 × 1109)	1662 (1 × 1662)	7049 (7 × 1007)
Expt. 5	3264 (8 × 408)	751 (1 × 751)	2520 (7 × 360)

[a] See end of the Experimental section for the definition of this value. [b] Not determined.

TABLE VIII

RADIOCHEMICAL AND DILUTION DATA FOR THE COMPOSITION OF THE AROMATIC HYDROCARBONS PRESENT IN THE HYDRO-ISOMERATE OBTAINED IN EXPERIMENT 4

Wt. of hydro-isomerate, g.	22.1113
Initial specific activity[a] of the C_8-aromatic hydrocarbons	54840 (8 × 6855)
Carrier hydrocarbon and wt., g.	
o-Xylene	0.8641
m-Xylene	.8569
p-Xylene	.8535
Aromatic acid and specific activity[a]	
o-Phthalic acid	2208 (8 × 276)
Isophthalic acid	3940 (10 × 394)
Terephthalic acid	1870 (10 × 187)

[a] See end of the Experimental section for the definition of this value.

ane to yield a near equilibrium mixture of alkylcyclohexane isomers. In addition, the results indicate that the alkylcyclopentane isomers, C_8H_{16}, are produced in a quantity to be expected from equilibrium considerations, although they were not investigated in any detail. The radioactivity distributions found in the dimethylcyclohexane isomers show that a deep-seated skeletal rearrangement must have taken place.

It had been established previously that saturated hydrocarbons undergo little isomerization in the presence of silica–alumina[17] nor do they isomerize when contacted with alumina–hydrochloric acid.[7] However, the corresponding olefinic hydrocarbons will undergo extensive isomerization and hydrogen disproportionation in the presence of alumina–hydrochloric acid and other metal oxide catalysts which possess "acidity."[7] It has been shown that alkenes such as pentenes are likewise isomerized in the presence of alumina treated with hydrofluoric acid.[18] It was also observed that at 330° platinized-alumina causes the dehydrogenation of 1,1,3-trimethylcyclohexane to *m*-xylene with liberation of methane. Whereas in the presence of a platinized-alumina–hydrogen chloride catalyst, skeletal isomerization accompanied dehydrogenation of 1,1,3-trimethylcyclohexane, and the aromatic hydrocarbons produced contained 32% 1,2,4- and 21% 1,2,3-trimethylbenzene.[19] When olefinic hydrocarbons were hydrogenated in the presence of nickel–silica–alumina catalyst, isomerization accompanied their reduction. The hydroisomerization occurred at lower temperatures than the corresponding saturated hydrocarbons reacted.[20] The presence of hydrogen is necessary for the composite catalysts, consisting of a hydrogenation component on an acidic support to function.[21]

The foregoing facts suggest that the hydro-isomerization of the ethylcyclohexanes in the presence of composite catalysts, which consist of a hydrogenation component and an acid support,[3,4,8] proceeds through a carbonium ion mechanism, similar to the one proposed for the skeletal isomerization of alkylcyclohexenes.[7] These carbonium ions may originate through the intermediate formation of alkenes or potential alkenes under the dehydrogenating influence of the catalyst and the subsequent combination of the alkenes with a proton. The acid component of the catalyst would be primarily responsible for the skeletal isomerization of the hydrocarbons. The function of the hydrogen may be to prevent the occurrence of side reactions and to keep the surface of the catalyst free of carbonaceous material.

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(17) G. M. Good, H. V. Voge and B. S. Greensfelder, *Ind. Eng. Chem.*, **39**, 1032 (1947); however, see S. G. Hindin, A. G. Oblad and G. A. Mills, *ibid.*, **77**, 535 (1955).

(18) A. G. Oblad, J. U. Messenger and H. T. Brown, *Ind. Eng. Chem.*, **39**, 1462 (1947).

(19) H. Pines, E. F. Jenkins and V. N. Ipatieff, THIS JOURNAL, **75**, 6226 (1953).

(20) F. G. Ciapetta, *Ind. Eng. Chem.*, **45**, 162 (1953).

(22) F. G. Ciapetta and J. B. Hunter, *ibid.*, **45**, 147 (1953).

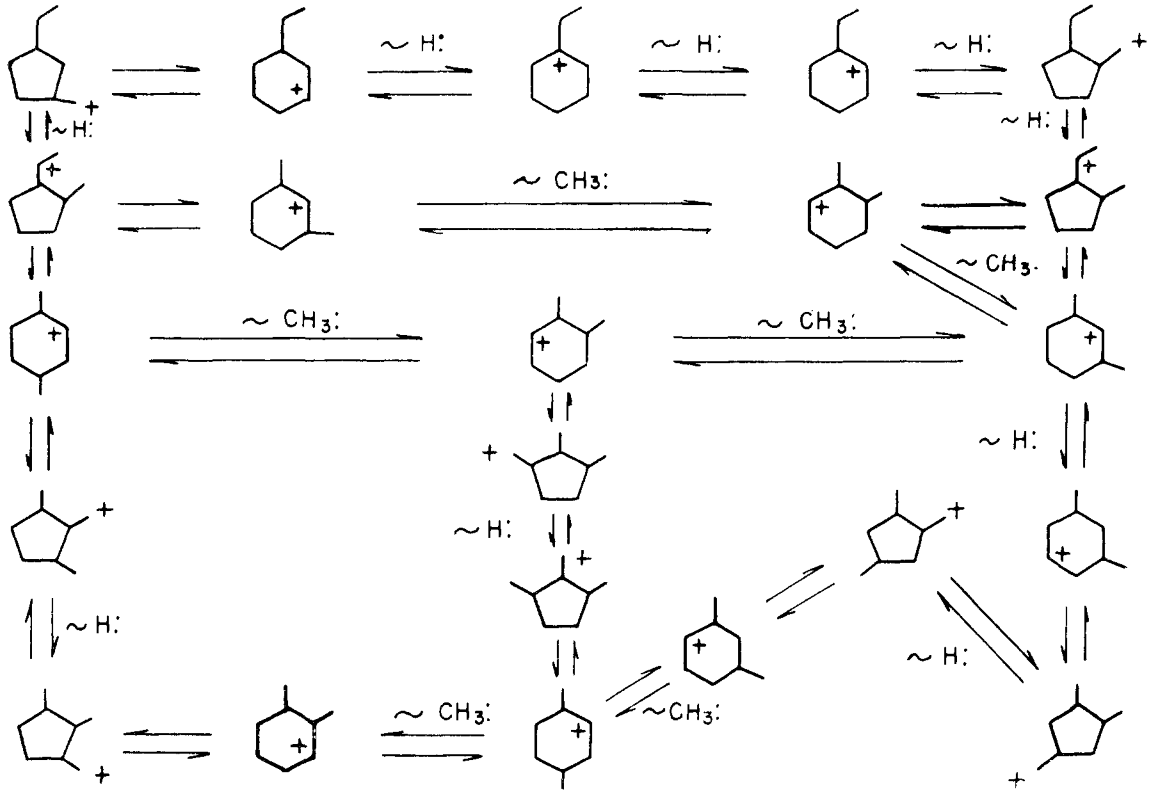

Diagram 2.—Schematic presentation of "scrambling" of carbon atoms in alkylcyclohexanes obtained from the hydroisomerization of ethyl-α- and β-cyclohexane.

It is not excluded, however, that the molecular hydrogen acts as a source of ionic hydrogens which facilitates the formation of carbonium ion. There is increasing physical[22] and chemical[23] evidence that hydrogen can be dissociated into ionic hydrogen on the surface of a nickel catalyst.

The results of the present study indicate that once the ethylcyclohexylcarbonium ion is generated, it may undergo a series of ring contractions and expansions, such as illustrated in Diagram 2. This diagram is not meant to imply that only the intermediates and the rearrangements outlined may occur, rather it merely illustrates how the carbon atoms may become scrambled. The carbonium ion chain may be terminated by one of many methods, such as an abstraction of a hydride ion from the surface of the catalyst or from another hydrocarbon molecule. In the latter event the new carbonium ion produced may undergo a similar series of rearrangements. The carbonium ions also may transfer a proton to the catalyst, and the olefins thus formed may then undergo hydrogenation to the corresponding cycloalkanes.

The observed extensive rearrangement of the carbon-14 isotope found in this study suggests that once the hydrocarbon molecule is activated by formation of the carbonium ion it may undergo many rearrangements before the chain is terminated. This seems likely in view of the fact that this reaction was performed in a flow system and repeated contact with the catalyst is, therefore, limited. It is not excluded, however, that the rearranged hydrocarbon molecule may enter into the carbonium ion mechanism more than once.

It is interesting to note that the concentration of the C^{14} in the ring of the dimethylcyclohexanes produced from ethyl-α-C^{14}-cyclohexane (expt. 3, Table V) is higher than the 75% concentration expected from an isotope equilibration, whereas the concentration of C^{14} in the ring of dimethylcyclohexanes obtained from the β-isomer is lower than the isotopic equilibration (Table V). These results are in line with the proposed mechanism. The primary dimethylcyclohexane carbonium ions obtained from ethyl-α-C^{14}-cyclohexane should contain the radioactive carbon in the ring only, while those obtained from the β-isomer should have the C^{14} on the side chain only, as indicated in Diagram 3. Repeated ring contractions and expansions are thus responsible for the almost statistical equilibration of the C^{14} between the ring and the side chain.

The carbonium ion chain reactions can terminate before such equilibration occurs, hence the difference in the distribution of the C^{14} in the dimethylcyclohexanes which were derived from the two isotopic isomers of ethylcyclohexane.

The presence of 1,1-dimethylcyclohexane in the hydro-isomerate was shown by the analytical scheme illustrated in Diagram 4. Although its concentration was not determined, the radioactivity distribution between the ring and the side chain indicated that essentially all of this isomer

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(22) L. E. Moore and P. W. Selwood, THIS JOURNAL, **78**, 697 (1956).

(23) H. Pines, M. Shamaiengar and W. S. Postl, *ibid.*, **77**, 5099 (1955).

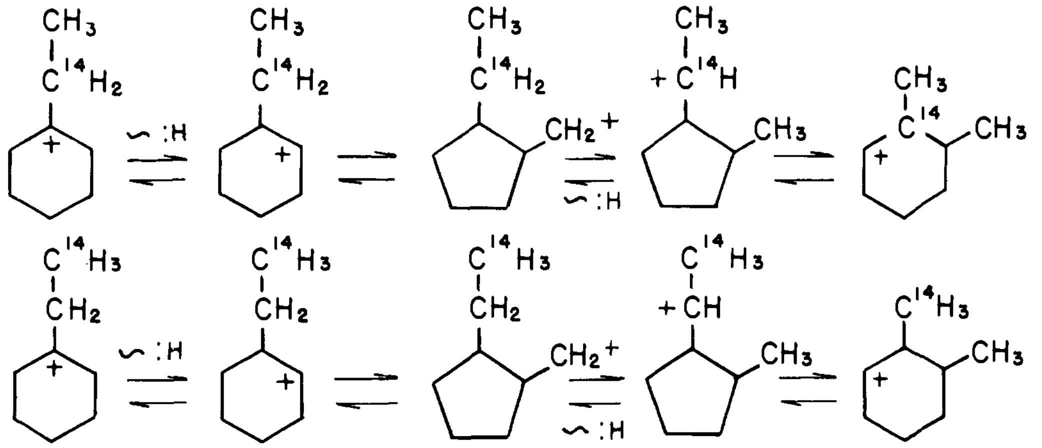

Diagram 3.—Primary dimethylcyclohexylcarbonium ions formed from the isomerization of ethyl-α- and β-C^{14}-cyclohexane.

arose by way of a mechanism similar to that described for the other dimethylcyclohexanes.

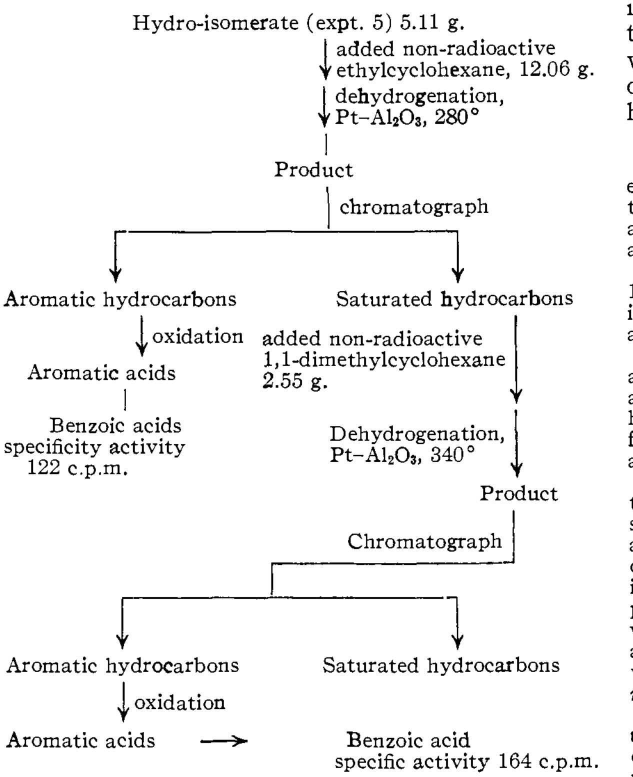

Diagram 4.—Procedure for the analysis of 1,1-dimethylcyclohexane

An alternative reaction path exists, whereby the extensive distribution of the C^{14} found in the dimethylcyclohexane isomers may be accounted for. This involves ring expansion from a six- to a seven-membered ring, followed by ring contraction to a six-membered ring. This type of ring expansion is considered less likely in view of previous work which has shown that there is little tendency for such reactions to occur *via* a carbonium ion mechanism. Pines, Shamaiengar and Postl[23] have reported the presence of methylcycloheptane derived from the reductive dehydroxylation of 1-methyl-1-hydroxymethylcyclohexane. The expansion from a six- to a seven-membered ring may have occurred because of the presence of a primary carbonium ion. In addition, a 1,2-hydride shift was not able to take place in this particular intermediate. It was found, however, that 1-cyclohexylethanol under the same conditions yielded no methylcycloheptane.[24]

Experimental

The yields reported in the syntheses are averages of several trial experiments with non-radioactive compounds. In the syntheses with radioactive materials, carriers were usually added directly to the reaction mixtures, and hence the actual yields were not determined.

Synthesis of Ethyl-α-C^{14}-cyclohexane.—A. **Acetic acid-1-C^{14}** was prepared from 25 mmoles of methylmagnesium iodide and 18.2 mmoles of radioactive barium carbonate, according to the published procedure[25]; yield 90%.

B. **(Aceto-1-C^{14})-phenone** was prepared from the acetic acid obtained above (diluted with 2.7 g. of non-radioactive acetic acid). The acetic acid was refluxed with 35 ml. of anhydrous benzene and 20 g. of anhydrous aluminum chloride for 8 hr. and the acetophenone was isolated and purified according to Brown and Neville[26]; yield 70%.

C. **Ethyl-α-C^{14}-cyclohexane** was prepared by reduction of the acetophenone obtained above (to which had been added sufficient inactive acetophenone to yield 19.82 g.). The acetophenone was dissolved in 30 ml. of *n*-pentane and reduced in a rotating autoclave using 4 g. of a catalyst consisting of 75% nickel–kieselguhr and 25% alumina, at an initial pressure of 120 atmospheres of hydrogen. The temperature was maintained at 150° until the pressure remained constant and the hydrogen uptake corresponded to the theoretical value. The ethyl-α-C^{14}-cyclohexane distilled at 131–132°, $n^{20}D$ 1.4323, yield 13.35 g., or 71.5% based on acetophenone.

Synthesis of Ethyl-β-C^{14}-cyclohexane.—A. **Cyclohexaneacetic Acid-carboxyl-C^{14}** was prepared from 44 mmoles of cyclohexylmethylmagnesium bromide and 37.3 mmoles of radioactive barium carbonate according to the usual procedure; yield 90%.

B. **Cyclohexaneëthanol-1-C^{14}** was prepared by dissolving the cyclohexaneacetic acid obtained above (to which had been added 20.2 g. of inactive cyclohexaneacetic acid) in dry ether and reducing with 12.0 g. of lithium aluminum hydride suspended in 500 ml. of ether; yield 80%.

C. **Ethyl-β-C^{14}-cyclohexane** was prepared by reductive dehydroxylation of the cyclohexane-ethanol obtained above.[23] The catalyst consisted of 4.0 g. of nickel–kieselguhr and 0.8 ml. of thiophene. The reaction was carried out at 150° in a rotating autoclave at an initial pressure of 100 atmospheres of hydrogen; b.p. 131–132°, $n^{20}D$ 1.4325, yield 1.5 ml., 90% based on cyclohexaneëthanol.

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(24) H. Pines and W. S. Postl, unpublished results.

(25) M. Calvin, C. Heidelberger, J. C. Reid, B. M. Tolbert and P. E. Yankwich, "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 178–179.

(26) W. G. Brown and O. K. Neville, Atomic Energy Commission, MDDC, 1168.

Catalyst Preparation.—The nickel–silica–alumina catalyst was prepared from 46.4 g. of $Ni(NO_3)_2 \cdot 6H_2O$ and 178 g. of ground silica–alumina (commercial cracking catalyst, Houdry S 45 type, containing 12% alumina) according to the published procedure.[21]

Before being used, the catalyst was pelleted ($^3/_{16} \times {}^1/_8$ inch). The catalyst pellets, 50 ml., were placed in the catalyst tube which was inserted in the furnace and activated in a stream of hydrogen (H_2 rate = 6 liters per hour) at atmospheric pressure and 520° for 16 hr.

The Flow Pressure Apparatus.—The apparatus used in this study was conventional. The hydrogen flowed through a Universal Oil Products electronic flowmeter to the top of the catalyst tube where it is joined by the ethylcyclohexanes whose rate was controlled by a proportioning pump provided with a variable rate adjustment. The ethylcyclohexane was charged to the pump from a 50-ml. glass buret. The hydrogen and ethylcyclohexane entered the top of the catalyst tube and passed over a spiral preheater and then over 50 ml. of the catalyst. The product passed through an air-cooled condenser and collected in a 100-ml. calibrated pressure receiver. The non-condensed product passed through a back pressure regulator, and was cooled in a water-cooled condenser. The gaseous product passed through a Dry Ice–acetone trap and then to a wet test meter. The furnace, preheater and catalyst bed temperatures were measured by means of iron–constantan thermocouples. There were two thermocouples located in the catalyst bed: one-third of the distance from the top and one-third of the distance from the bottom of the bed.

The Hydro-isomerization Reaction.—After the catalyst had been activated, the furnace temperature was adjusted to give an average catalyst bed temperature of 360°. The unit was brought to 25 atmospheres, and the hydrogen flow adjusted to 4 moles of hydrogen per mole of hydrocarbon. The feed pump was started and inactive ethylcyclohexane was passed over the catalyst while the hourly liquid space velocity and temperature were adjusted.

When the desired experimental conditions had been reached, inactive cyclohexane was pumped over the catalyst until only a few ml. remained in the charging buret. Then the liquid product was withdrawn from the high pressure receiver and radioactive ethylcyclohexane added to the charging buret. After almost all of the radioactive ethylcyclohexane had been passed over the catalyst, more inactive ethylcyclohexane was added to the charging buret. Samples were withdrawn from the high pressure receiver periodically. The samples were identical except for their level of radioactivity. Negligible amounts of product were obtained in the water-cooled atmospheric pressure trap and the Dry Ice–acetone trap. Only the reaction product collected in the pressure receiver was analyzed.

Experiments 1, 2 and 3 were made with the α- and experiments 4 and 5 with the β-ethyl-C^{14}-cyclohexane.

Analysis of the Hydro-isomerate.—Experiment 1 was performed in order to determine whether any isomerization occurred during the analysis. A portion of the synthesized ethyl-α-C^{14}-cyclohexane which was not contacted with the nickel–silica–alumina catalyst was subjected to the analytical scheme. It was found that no isomerization occurred during analysis and that only negligible radioactivity was located in the ring of the ethylcyclohexane.

In addition a portion of the synthesized ethyl-β-C^{14}-cyclohexane was dehydrogenated and oxidized. The benzoic acid thus obtained contained no radioactivity. Hence, all of the radioactivity was located in the β-carbon atom.

Since all the experiments were performed and analyzed in essentially the same manner, only one experiment will be described in detail. Experiment 5 will be described because both the isotope dilution analysis and the securing of the aromatic acids for degradation were performed upon a single portion of the hydro-isomerate. In some experiments two samples of the hydro-isomerate were worked up separately. However, the samples were identical in every respect except for their level of radioactivity.

In experiment 5, 12 ml. of ethyl-β-C^{14}-cyclohexane with a specific activity of 57640 c.p.m. was charged into the flow pressure system under the reaction conditions given in Table I.

Successive samples were withdrawn from the high pressure receiver periodically. To 10.8030 g. of hydro-isomerate, $n^{20}D$ 1.4288, specific activity 13363 c.p.m., were added 1.5635 g. of 1,2-dimethylcyclohexane, 1.5301 g. of 1,3-dimethylcyclohexane and 1.5276 g. of 1,4-dimethylcyclohexane. The homogeneous mixture was chromatographed over 60–200 mesh silica gel (column length 170 cm., containing 500 ml. of gel), using absolute ethanol as eluent. The recovered saturated hydrocarbons 13.80 g., $n^{20}D$ 1.4279, which showed a negative test for aromatics by means of the formaldehyde–sulfuric acid color test, were passed over 20 ml. of platinized-alumina catalyst at 280° and H.L.S.V. of 0.5. There were 5.7 liters of hydrogen evolved. The product, $n^{20}D$ 1.4664, was chromatographed as before. The recovered aromatic hydrocarbons, 5.75 g., $n^{20}D$ 1.4970, were oxidized with potassium permanganate according to Norris and Vaala.[27] The manganese dioxide was removed by filtration, washed with hot water and the filtrate and washings combined and acidified with hydrochloric acid. After cooling to room temperature, the precipitated terephthalic and isophthalic acids, 2.0570 g., were separated by filtration.[28] The filtrate was made alkaline with sodium hydroxide, concentrated to 175 ml. and acidified with hydrochloric acid. When cooled in an ice–water-bath, benzoic acid, 0.95 g., precipitated and was recovered by filtration. The filtrate was extracted with ether in a continuous liquid–liquid extractor for 48 hr. The ether was evaporated leaving 2.0 g. of residue, which was treated with two portions of chloroform, 25 ml. and 10 ml., to dissolve benzoic acid from *o*-phthalic acid. The crude *o*-phthalic acid thus isolated amounted to 1.4 g.

The mixture of terephthalic and isophthalic acids, 2.0570 g., was separated by the method of Smith.[29] The terephthalic acid, 0.69 g., was purified by repeated recrystallization of its dimethyl ester from an alcohol–water mixture. The isophthalic acid, 1.3031 g., was further purified by treatment with aqueous thallous acetate according to Bryce-Smith.[30] In this experiment, the isophthalic acid obtained was scavenged with an equal weight of inactive terephthalic acid in order to remove the contaminating radioactive terephthalic acid. The same method was used in experiment 4; however, in experiments 1, 2 and 3, the isophthalic acid was purified by repeated recrystallization of the dimethyl ester from an alcohol–water mixture.

The crude benzoic acid, 0.95 g., was dissolved in 25 ml. of chloroform, filtered and the filtrate evaporated. The precipitate, after repeated recrystallization from water, weighed 0.4404 g., m.p. 121–122°.

The crude *o*-phthalic acid, 1.4467 g., was refluxed with 3.0 g. of thionyl chloride for 1 hr.,[31] followed by the addition of 25 ml. of carbon tetrachloride. The precipitate obtained was recrystallized repeatedly from carbon tetrachloride. Phthalic anhydride, 0.1727 g., m.p. 130–131°, was obtained.

The pure acids were burned in a semi-micro combustion tube and the carbon dioxide taken up in sodium hydroxide and precipitated and assayed as barium carbonate. The results are summarized in Tables II and III.

Decarboxylation of the Aromatic Acids.—**A. Decarboxylation of the benzoic, terephthalic and isophthalic acids** obtained above was carried out according to the procedure outlined by Calvin, *et al.*,[32] using copper oxide catalyst and redistilled quinoline. In most experiments the aromatic acid was diluted with the corresponding inactive acid in order to allow a larger quantity of material to be handled. A nitrogen sweep carried the benzene into a Dry Ice-trap and the carbon dioxide evolved was collected in sodium hydroxide, precipitated as barium carbonate and assayed. A portion of the benzene was burned and the carbon dioxide converted to infinitely thick barium carbonate samples, which were then assayed.

B. **Decarboxylation of *o*-phthalic acid** was carried out by means of the Schmidt reaction.[33] The phthalic anhydride obtained above was diluted with inactive phthalic anhydride and the mixture treated with 10% hydrochloric acid in order to yield 1.0 g. of the acid. The Schmidt reaction was performed in a manner similar to that described by Roberts,

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[27] J. F. Norris and G. T. Vaala, THIS JOURNAL, **61**, 2131 (1939).

[28] H. Gilman and J. E. Kirby, *ibid.*, **54**, 351 (1932).

[29] M. E. Smith, *ibid.*, **43**, 1920 (1921).

[30] D. Bryce-Smith, *Chemistry & Industry*, 244 (1953).

[31] W. H. Stevens and D. A. Holland, *Science*, **112**, 718 (1950).

[32] Ref. 22, pp. 229–230.

[33] M. Von Oesterlin, *Z. angew. Chem.*, **45**, 536 (1932).

Lee and Saunders.[34] The carbon dioxide evolved was swept into sodium hydroxide with nitrogen and precipitated as barium carbonate. The reaction mixture in the flask was transferred to a separatory funnel and the sulfuric acid layer withdrawn onto 50 g. of wet ice. Sufficient sodium hydroxide solution was used to neutralize the sulfuric acid and then 10 ml. of glacial acetic acid was introduced, followed by copper acetate according to the published procedure.[35] The copper anthranilate obtained was suspended in water, and hydrogen sulfide bubbled into the suspension for 1 hr. The solution was filtered to remove the copper sulfide produced and the filtrate extracted with four 100-ml. portions of ether and the latter evaporated. The residue was decolorized with charcoal and repeatedly recrystallized from ligroin (b.p. 86–100°). The anthranilic acid, 0.0725 g., m.p. 144–145°, was burned to carbon dioxide and assayed as barium carbonate.

The radiochemical assay data from all experiments are summarized in Tables VI and VII, and the percentage radioactivity distribution between ring and side chain of the dimethylcyclohexane isomers are reported in Table V.

Determination of the Radioactivity of the C_8-Cycloalkanes in the Hydro-isomerate.—In the reactions performed using ethyl-α-C^{14}-cyclohexane, the initial radioactivity of the C_8-cycloalkanes in the product were determined by calculation from the activity of the benzoic acid obtained during analysis of the hydro-isomerate.

In the hydro-isomerization of ethyl-β-C^{14}-cyclohexane, it was found that when a portion of the hydro-isomerate was burned and assayed, this value agreed within the limits of the experimental counting error, with the actual radioactivity found in the C_8-cycloalkanes by isolation and assay of a phthalic acid.

Determination of the Conversion of the Ethylcyclohexane.—When ethyl-α-C^{14}-cyclohexane was the charging stock, the conversion was obtained by comparing the radioactivity of the benzoic acid derived from the hydro-isomerate after dilution with a known weight of inactive ethylcyclohexane with the radioactive benzoic acid obtained from the same sample of hydro-isomerate before dilution.

In those experiments where ethyl-β-C^{14}-cyclohexane was used as the charging stock, *p*-ethylbenzoylpropionic acid[36] was prepared from the ethylbenzene obtained by dehydrogenation, before and after addition of inactive ethylcyclohexane to the hydro-isomerate. The derivatives were assayed for radioactivity and the results are given in Table III.

The portion of the ethylcyclohexane present which had undergone reaction was calculated from a consideration of the amount of radioactivity found in the ring of benzoic acid. The assumption is made that the ethylcyclohexane entering into the isomerization reaction would undergo an isotope position rearrangement to the same extent as the other isomers. Justification for this assumption may be had by an examination of the radioactivity distribution found in benzoic acid derived from the hydro-isomerates of experiments 4 and 5, Table VI.

The calculation may best be illustrated by a specific example. In experiment 2, the radiochemical assay data (Table VI) for the decarboxylation of benzoic acid indicate that 4.1% of the radioactivity is located in the ring. Since the other isomers have a radioactivity distribution between the ring and side chain of about 75:25, the assumption is made that this would be the radioactivity distribution of the reacted ethylcyclohexane if it were not diluted with unreacted ethylcyclohexane. Therefore, the proportion 4.1 : x = 75:100, when solved for x, gives the percentage of the ethylcyclohexane which had reacted. This value is 5.47%. Since the percentage of ethylcyclohexane present in the hydro-isomerate is 59.9%, then (0.0547) (59.9) equals 3.3% of reacted ethylcyclohexane is present in the hydro-isomerate. The results of the calculations for the conversion of ethylcyclohexane are summarized in Table I.

The Concentration of the Alkylcyclohexanes in the Hydro-isomerate.—The calculation of the concentration of the alkylcyclohexanes present in the hydro-isomerate may best be illustrated by a sample calculation for the 1,2-dimethylcyclohexane found in experiment 5. In the equation[37]

$$\frac{X + Y}{X} = \frac{S_1}{S_2}$$

S_1 = specific activity of the undiluted 1,2-dimethylcyclohexane, 13, 363 c.p.m.

S_2 = specific activity of the diluted 1,2-dimethylcyclohexane, determined by the assay of phthalic anhydride, specific activity 2232 c.p.m.

X = weight of the 1,2-dimethylcyclohexane of specific activity 13363 c.p.m.

Y = weight of non-radioactive 1,2-dimethylcyclohexane added, 1.5635 g.

then

$$\frac{X + 1.5635}{X} = \frac{13363}{2232}$$

$$X = 0.313 \text{ g.}$$

The weight of the sample of hydro-isomerate was 10.8030 g. Therefore 0.313/10.8030 × 100 = 2.9% of the hydro-isomerate consisted of 1,2-dimethylcyclohexane.

In this manner the concentration of the alkylcyclohexane isomers in the hydro-isomerate were calculated from the data in Tables II and III and the results are summarized in Table I.

The radioactivity distribution between the ring and side chain of the dimethylcyclohexane isomers were determined directly from the data reported in Tables VI and VII. For example, the specific activity obtained for the carbon dioxide and benzene derived from isophthalic acid of experiment 2 was 168 and 212 c.p.m., respectively. The isophthalic acid had a specific activity of 206 c.p.m. After correcting for dilution by the non-tagged carbon atoms, the following results are obtained

$$\frac{(2)(168)}{(8)(206)} \times 100 = 20\% \text{ of the radioactivity was located in the side chain}$$

$$\frac{(6)(212)}{(8)(206)} \times 100 = 77\% \text{ of the radioactivity was located in the ring}$$

Examination of the Hydro-isomerate for the Presence of Alkylcyclopentane Isomers.—In the radioactive experiments, the hydroisomerate was not exhaustively dehydrogenated. Rather, the chief aim was to secure by selective dehydrogenation only sufficient aromatic hydrocarbons in order that they could be assayed and degraded, after conversion to the corresponding aromatic acids.

However, in several trial runs with non-radioactive ethylcyclohexane as the starting material, the hydro-isomerate was exhaustively dehydrogenated until no further aromatic hydrocarbons could be produced. The dehydrogenation product was chromatographed over silica gel to remove the aromatic hydrocarbons formed and the following refractive indices were obtained for the saturated hydrocarbons.

Expt.	No. of times hydro-isomerate[a] passed over $Pt-Al_2O_3$ at 280°	H.L.S.V.	$n^{20}D$ of satd. hydrocarbons
6	3	0.5	1.4196
7	4	.5	1.4190
8	5	.5	1.4210

[a] The hydro-isomerization reactions were performed under reaction conditions identical with experiments 2, 3 and 4.

Examination of the Hydro-isomerate of Experiment 5 for the Presence of 1,1-Dimethylcyclohexane.—A portion, 10.1281 g., of the hydro-isomerate from experiment 5 containing 0.7639 g. of inactive 1,1-dimethylcyclohexane was chromatographed over 60–200 mesh silica gel (500 ml.) and eluted with absolute ethanol. The saturated hydrocarbons, 9.78 g., $n^{20}D$ 1.4388, were passed over the platinized-alumina catalyst, 20 ml., at an H.L.S.V. of 0.4 at 280°. The hydrocarbons were passed twice over the catalyst and a total of 2.9 l. of hydrogen was evolved. The product, $n^{20}D$ 1.4540, was separated into aromatic and saturated hydrocarbons as before. The aromatic hydrocarbons were oxidized and benzoic acid was isolated, purified and assayed;

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[34] J. D. Roberts, C. C. Lee and W. H. Saunders, THIS JOURNAL, **76**, 4501 (1954).

[35] W. M. Cumming and I. V. Hopper, "Systematic Organic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1924, p. 292.

[36] J. R. Reinheimer and S. Taylor, *J. Org. Chem.*, **19**, 802 (1949).

[37] H. J. Schaeffer and C. J. Collins, THIS JOURNAL, **78**, 133 (1955).

specific activity 404 c.p.m. The specific activity of the benzoic acid obtained from another portion of the same sample of hydro-isomerate from experiment 5 was 393 c.p.m. Therefore, the two values agree to within 3%. If all or part of the radioactivity of the benzoic acid had been derived from the toluene produced by the demethanation of 1,1-dimethylcyclohexane, its radioactivity would have been markedly lowered by the addition of non-radioactive 1,1-dimethylcyclohexane.

The saturated hydrocarbons, 5.11 g., n^{20}D 1.4320, obtained from the preceding chromatographic separation were combined with 12.06 g. of non-radioactive ethylcyclohexane, n^{20}_{D} 1.4325. The material was analyzed as illustrated in Diagram 2. Since the specific activity of the benzoic acid was increased substantially by this procedure, a new species of this acid probably arose by way of the aromatization of 1,1-dimethylcyclohexane, which would lead to toluene and, upon oxidation, to benzoic acid.

The benzoic acid containing the new isotopic species was decarboxylated as before. The carbon dioxide evolved was absorbed in aqueous sodium hydroxide, precipitated as barium carbonate and assayed; specific activity 447 c.p.m.

The benzene obtained from the decarboxylation reaction was purified, burned and assayed; specific activity 114 c.p.m.

Validity of the Analytical Scheme.—The dehydrogenation step was conventional, utilizing platinized-alumina catalyst which had been tested for "acidity" with 1,1,3-trimethylcyclohexane and found to cause no noticeable amount of isomerization.[19]

The oxidation product of *o*-xylene was examined in order to determine whether benzoic acid was produced from this hydrocarbon under conditions of potassium permanganate oxidation.[38] *o*-Xylene, 4.2 ml. (Eastman Kodak Co., White label, n^{20}D 1.5024) was oxidized with potassium permanganate as described previously. After removing the manganese dioxide by filtration, the filtrate was combined with 0.366 g. of radioactive benzoic acid having a specific activity of 2456 c.p.m. The solution was alkaline and, therefore, the mixture of acids was homogenized. The benzoic acid was re-isolated and purified as before and assayed; specific activity 2401 c.p.m. Therefore only a negligible quantity of benzoic acid was produced in this oxidation.

In order to determine the purity of the benzoic acid obtained by repeated recrystallization from water, the following experiment was performed. Radioactive benzoic acid, 0.1188 g., derived from the hydro-isomerate of experiment 4 having a specific activity of 363 c.p.m. was sublimed twice at 100° and atmospheric pressure. A portion of the sublimate was burned and assayed, specific activity 362 c.p.m. Therefore, benzoic acid purified by repeated recrystallization was not contaminated with traces of isophthalic acid (or any toluic acid) because extensive fractionation of the radioactivity would have occurred upon sublimation at 100° and atmospheric pressure.

The radioactivity assays reported in this paper were performed with a Nuclear Instruments Co.[39] No. 162 Scaling Unit and a Tracerlab-TGC-2 Geiger–Müller tube.[40] For convenience, each counting rate reported in this work is referred to as "Specific Activity," which is defined as the number of counts per minute above background, corrected for coincidence losses, of an "infinitely thick" layer of barium carbonate, 4.52 cm.^{2} in area. Each value reported is the average of at least two determinations. The individual counting rates were known to an accuracy of 3%. In order to permit a ready comparison of the radioactivities of different compounds, the specific activities reported in the tables were multiplied by the number of carbon atoms in the compound to correct for dilution by non-tagged carbon atoms.

Acknowledgment.—The authors are indebted to Dr. H. M. Neumann for his assistance in the work with C^{14}-labeled compounds.

[38] M. S. Nemtsov and F. S. Shenderovich, *Khim. Tverdogo Topliva*, **6**, 729 (1935); *C. A.*, **31**, 1379 (1937).

[39] Nuclear Instrument and Chemical Corporation, 223 W. Erie St., Chicago, Ill.

[40] Tracerlab, Inc., 130 High St., Boston, Mass.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Synthesis of 2,7-Disubstituted Tropones *via* Aromatization

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A new method is here reported for the synthesis of tropones, specifically those substituted with similar aralkyl groups in the 2- and 7-positions. The general method involves the isomerization and dehydrogenation of substituted 2,7-dibenzylidenecycloheptanones to the correspondingly substituted 2,7-dibenzyltropones in boiling triethylene glycol solution using palladium-on-charcoal.

The successful employment of palladium-on-charcoal in a refluxing glycol solvent for the synthesis of substituted γ-pyrones,[3] γ-pyridones[4] and tropolones[5] by isoaromatization suggested that a similar method might produce substituted tropones. In the isoaromatization conversions realized previously, the number of multiple linkages in precursor and product was identical. For the conversion of type I to type II to be effected, it would obviously be necessary to introduce one double bond in addition to those isomerized. We were led to expect that the process might be feasible because of the dehydrogenations and the disproportionations known to take place using palladium catalyst and heat[6] and because of the recognized aromatic nature of the tropone nucleus.[7,8]

2,7-Dibenzylidenecycloheptanone (Ia) and similar compounds in the series (Ib-l) were made by the method of Cornubert, Joly and Strébel,[9] with modifications in the purification procedure depending upon the particular 2,7-disubstituted cy-

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[1] Eli Lilly and Company Fellow, 1953–1954.

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[3] N. J. Leonard and D. Choudhury, THIS JOURNAL, **79**, 156 (1957).

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[9] R. Cornubert, R. Joly and A. Strébel, *Bull. soc. chim. France*, [5] **5**, 1501 (1938).