Alumina: Catalyst and Support. XXXVI.[1] 1,2-, 1,3-, and 1,4-Phenyl Migrations in 1-Methyl-1-phenylcyclohexane. Dehydroisomerization of 1-Methyl-C^{14}-1-phenylcyclohexane over "Nonacidic" Chromia–Alumina[2,3]

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The dehydroisomerization of 1-methyl-1-phenylcyclohexane over "nonacidic" chromia–alumina was studied using a pulse microreactor. *o*-, *m*-, and *p*-phenyltoluene were formed in addition to fission products. Carbon-14 tracer studies showed that *o*- and *p*-phenyltoluene were formed almost exclusively by 1,2- and 1,4-phenyl migrations, respectively. The *meta* isomer was produced by 1,3-phenyl migration to the extent of 67% and about 30% by a thermal ring opening, followed by hydrogen transfer and a concerted ring closure. Approximately 3% of each isomer was produced by ring expansion *via* methyl insertion with subsequent contraction. Free-radical species are proposed as intermediates in the mechanisms suggested.

It has been shown that the nature of chromia–alumina catalysts depends upon the type of alumina used.[4] The properties of the alumina vary with its method of preparation. Alumina obtained from potassium aluminate (alumina-B) is of low acidity[5] and is used as the support for "nonacidic" chromia–alumina-B.

There is evidence that this catalyst promotes reactions of a radical nature rather than those of a cationic type, which are associated with "acidic" chromia–alumina-A (alumina from aluminum isopropoxide). For example, there was no cationic-type isomerization *via* methide migration when 1,1-dimethylcyclohexane was passed over chromia–alumina-B, since toluene and methane were the only products.[6] Further, isobutylbenzene was obtained from *t*-butylbenzene over this catalyst,[2] which also occurred when radical sources were decomposed in *t*-butylbenzene.[7]

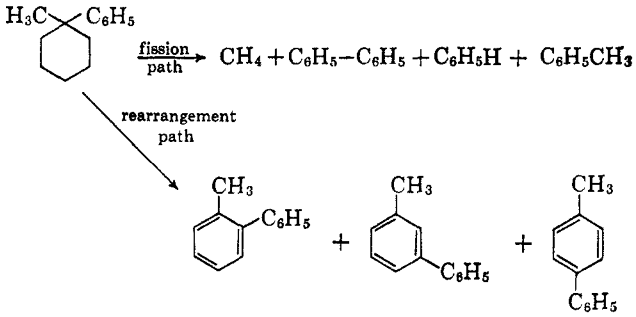
The involvement of free-radical intermediates during reactions promoted by this catalyst was also consistent with the production of *o*- and *p*-terphenyl by 1,2- and 1,4-phenyl migrations during the dehydroisomerization of 1,1-diphenylcyclohexane.[1] The present study of 1-methyl-1-phenylcyclohexane was intended therefore as an extension of the investigation of possible phenyl migrations promoted by chromia–alumina-B.

However, a preliminary investigation using the pulse microreactor showed a different distribution (*ortho*:*meta*:*para*) of isomerized products compared with that found for 1,1-diphenylcyclohexane. Therefore the carbon-14 distribution in the products from the large-scale dehydroisomerization of 1-methyl-C^{14}-1-phenylcyclohexane was determined to elucidate their mechanism of formation.

Discussion of Results

The dehydroisomerization of 1-methyl-1-phenylcyclohexane over chromia–alumina-B in the pulse microreactor at temperatures between 325 and 423°

SCHEME I



yielded methane, biphenyl, benzene, toluene, and *o*-, *m*-, and *p*-phenyltoluene (Scheme I). No reaction occurred over glass beads.

Supplementary experiments, analogous to those for 1,1-diphenylcyclohexane,[1] were performed to establish that the rearranged products were essentially primary ones resulting from intramolecular reaction: (a) *o*-, *m*-, and *p*-phenyltoluene did not rearrange under the reaction conditions; (b) possible precursors of the rearranged products, namely, *o*-, *m*-, and *p*-methylphenylcyclohexane, underwent negligible rearrangement under the reaction conditions with dehydrogenation as the main reaction. Further, intermolecular phenylation is unlikely since a solution of biphenyl in benzene did not yield any terphenyls[1] and they were not formed here from 1-methyl-1-phenylcyclohexane although biphenyl is a major product.

The results from the preliminary investigation utilizing the pulse microreactor are shown in Table I. The pronounced temperature dependence of the formation of *o*-phenyltoluene is parallel to that for the 1,2-phenyl migration in 1,1-diphenylcyclohexane to yield *o*-terphenyl.[1] This result supports the suggestion made then that the transition state for 1,2-phenyl migration may be congested and involves a species similar to that already invoked[8] for such migrations *via* a radical intermediate. The formation of *p*-phenyltoluene also might be by a direct phenyl migration, namely, 1,4-, which is supported by the lack of secondary phenyl migrations.

The possibility that these rearranged products arose by a methyl migration probably can be ruled out since ethylbenzene and xylenes were not obtained when 1,1-dimethylcyclohexane was passed over this catalyst.[6]

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[1] For paper XXXV, see H. Pines, W. F. Fry, N. C. Sih, and C. T. Goetschel, *J. Org. Chem.*, **31**, 4094 (1966).

[2] Paper XIX in the series Aromatization of Hydrocarbons. For paper XVIII, see H. Pines and C. T. Goetschel, *J. Am. Chem. Soc.*, **87**, 4207 (1965).

[3] This research was supported by the Atomic Energy Commission Contract AT(11-1)-1196.

[4] C. T. Chen, W. O. Haag, and H. Pines, *Chem. Ind.* (London), 1379 (1959).

[5] H. Pines and W. O. Haag, *J. Am. Chem. Soc.*, **82**, 2471 (1960).

[6] H. Pines and C. T. Chen, *ibid.*, **82**, 3562 (1960).

[7] H. Pines and C. N. Pillai, *ibid.*, **82**, 2921 (1960); L. H. Slaugh and J. H. Raley, *ibid.*, **82**, 1259 (1960); **84**, 2640 (1962).

[8] For literature pertaining to phenyl migration, see ref 1, footnotes 7b, 8, 9, 10, 11, and 12.

TABLE I

THE EFFECT OF TEMPERATURE UPON THE DEHYDROISOMERIZATION OF 1-METHYL-1-PHENYLCYCLOHEXANE OVER CHROMIA–ALUMINA-B

Expt	1	2	3	4	5	6
Temp, °C	280	300	325	377	403	423
Conversion,[a] mole %	2.7	6.6	13.4	24.5	30.1	30.0
Product compn, mole %						
Methane	Not estd					
Benzene	22.5	16.1	14.0	11.9	11.3	8.6
Toluene	25.3	19.8	17.5	13.1	12.3	10.4
Biphenyl	34.7	38.0	50.0	59.9	64.0	65.8
o-Phenyltoluene	0.0	Trace	1.3	1.4	1.4	1.6
m-Phenyltoluene	28.1	22.5	18.0	17.1	13.5	13.0
p-Phenyltoluene	12.0	9.9	8.9	8.6	6.5	6.9
Unknown	Not estd		4.3	Not estd	2.3	2.4
Ratio of *o*-/*p*-phenyltoluene	0.0	0.0	0.15	0.16	0.22	0.23
Ratio of *m*-/*p*-phenyltoluene	2.3	2.3	2.0	2.0	2.1	1.9

[a] Isodurene was used as an internal standard.

However, it is not certain that these products are the result solely of direct phenyl migration, particularly *m*-phenyltoluene, since 1,1-diphenylcyclohexane gave virtually no *m*-terphenyl. The presence of the methyl group might be facilitating ring expansion or ring-opening and -closing mechanisms; so the products from the dehydroisomerization of 1-methyl-C^{14}-1-phenylcyclohexane were assayed.

Investigation of the reaction with the microreactor had shown that maximum conversion was between 400 and 425° and after exploratory runs with inactive material the upper temperature was chosen. Therefore, 1-methyl-C^{14}-1-phenylcyclohexane was dehydrogenated at 422° over "nonacidic" chromia–alumina-B in a conventional, vertical, continuous-flow apparatus.[9] The reaction conditions and the composition of the product are summarized in Table II.

TABLE II

DEHYDROISOMERIZATION OF 1-METHYL-C^{14}-1-PHENYLCYCLOHEXANE OVER CHROMIA–ALUMINA-B

Duration of expt, min	91.0
Total feedstock passed, ml	8.1
Amt of catalyst	17.3 g, 19 cc
Temp, °C	422
H.L.S.V.	0.28
Recovery, mole %	90
Conversion, mole %	48
Composition of hydroisomerate, mole %	
Methane	Not estd
Benzene	2.8
Toluene	3.8
Biphenyl	63.1
Diphenylmethane	7.5
o-Phenyltoluene	7.3
m-Phenyltoluene	8.3
p-Phenyltoluene	10.0

Diphenylmethane was observed in the product when this procedure was used and it may be that the passage of a relatively large amount of hydrocarbon compared to the microreactor is responsible by modifying the catalyst with carbonaceous material.

Owing to the minute amounts of benzene and toluene produced, these were diluted in the reaction mixture by adding known amounts of the inactive compounds before the products were separated by preparative gas chromatography. The benzene and biphenyl were assayed directly (Table III), but the toluene, diphenylmethane, and the phenyltoluenes were diluted with the corresponding inactive compounds before being oxidized to the respective benzoic or phenylbenzoic acids.

TABLE III

DILUTION OF BENZENE AND RADIOACTIVITIES OF BENZENE AND BIPHENYL FROM THE DEHYDROISOMERIZATION OF 1-METHYL-C^{14}-1-PHENYLCYCLOHEXANE

Dilution data	
Benzene formed,[a] g	0.05
Benzene added,[b] g (diln 1)	0.20160
Benzene recovered, g	0.09342
Benzene added,[c] g (diln 2)	0.21328
Activities, µCi/mmole	
Recycled benzene (measd)	0.0375
Original benzene (calcd)	0.62
Biphenyl (measd)	0.185

[a] Estimated from vpc trace of product mixture using isodurene as an internal standard and is therefore an approximate figure. [b] Added for ease of handling and collection during preparative vpc separation from reaction mixture. [c] Added since the benzene recovered was not quite pure and was recycled through vpc column.

These acids were decarboxylated with boiling quinoline and copper oxide. The benzene or biphenyl and carbon dioxide produced were collected separately and assayed for radioactivity. Tables IV and V summarize the radioactivities of the aromatic acids and their products of decarboxylation. Usually the differences between the radioactivities of the acids and the sums of the radioactivities of their products of decarboxylation were less than ±3%.

TABLE IV

DECARBOXYLATION OF BENZOIC ACID FROM TOLUENE AND DIPHENYLMETHANE

	Toluene	Diphenylmethane
Acid decarboxylated, mmoles	0.75	1.60
Barium carbonate obtained, mmoles	0.51	1.26
Benzene obtained, mmoles	0.44	1.04
Barium carbonate yield, mole %	68	79
Benzene yield, mole %	59	65
Radioactivities, µCi/mmole		
Starting acid	0.630	1.78
Barium carbonate	0.620	1.66
Benzene	0[a]	0[a]
Radioactivities, %		
In the side chain	98.4	93.2
In the ring	0	0
Difference	−1.6	−6.8

[a] There may have been a slight activity but at the most only twice the background so regarded as immeasurable.

That more than 93% of the radioactivity in the *o*- and *p*-phenyltoluene is in the side chain (methyl group) shows that these compounds are formed mainly by direct 1,2- and 1,4-phenyl migration, respectively, as already suggested and probably involve species analogous to those previously proposed.[1] The 1,4 migration invokes the boat form of cyclohexane and the advantageous geometry of the sp^2 hybridization of carbon 4. However, a small amount of radioactivity, about 3%, is found in the ring, showing that other mechanisms are

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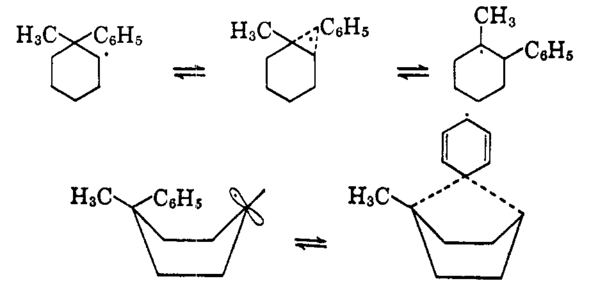
(9) H. Pines and S. M. Csicsery, *J. Catalysis*, **1**, 313 (1962).

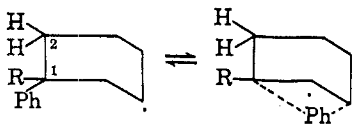
TABLE V
DECARBOXYLATION OF PHENYLBENZOIC ACIDS FROM PHENYLTOLUENES

	ortho acid	*meta* acid	*para* acid
Acid decarboxylated, mmoles	0.85	1.11	1.29
Barium carbonate obtained, mmoles	0.66	0.96	1.14
Biphenyl obtained, mmoles	0.57	0.78	1.15
Barium carbonate yield, mole %	78	87	88
Biphenyl yield, mole %	67	70	89
Radioactivities, μCi/mmole			
Starting acid	4.41	1.45	3.69
Barium carbonate	4.11	0.954	3.57
Benzene	0.112	0.475	0.111
Radioactivities, %			
In the side chain	93.2	65.8	96.8
In the ring	2.5	32.8	3.0
Difference	−4.3	−1.4	−0.2



operating. This is particularly noticeable in the case of the *m*-phenyltoluene where the radioactivity in the ring is about 33%, *i.e.*, at least ten times greater than in the *ortho* and *para* isomers. Nevertheless, the majority of the carbon-14 is retained in the methyl group, indicating that a 1,3-phenyl migration is occurring. If the proposal of radical intermediates is correct, this appears to be the first instance of a 1,3-phenyl migration in a radical species. No such migration was observed in 3-phenyl-1-C^{14}-propyl radical.[10]

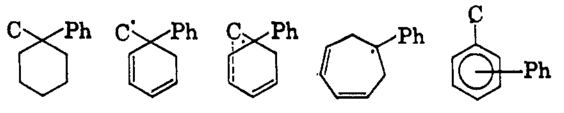
1,1-Diphenylcyclohexane did not undergo a 1,3-phenyl migration[1] and it may be that this is due to steric factors. The skew–boat form of the cyclohexane ring would allow 1,3 migration and possibly 1-methyl-1-phenylcyclohexane can achieve this configuration since



the substituent R on carbon 1 is nearly eclipsed by the hydrogen as carbon 2 and this steric interaction is less severe when R is a methyl group rather than a phenyl group.

For the insertion of carbon-14 into the ring, two mechanisms are possible. The first probably accounts for the small amount of radioactivity found in the ring in the *o*- and *p*-phenyltoluene and for part of that in the *m*-phenyltoluene.

Insertion might occur with initial partial dehydrogenation of the cyclohexane ring to yield a cyclohexene or cyclohexadiene species in which the formation of a radical on the methyl carbon is facilitated, although it is a primary radical, by the proximity of the phenyl ring and the double bond(s). Subsequent methyl insertion by a vinyl migration would yield a benzylic radical in a seven-membered ring. Collapse of this seven-membered ring could yield the phenyltoluenes. Ring ex-

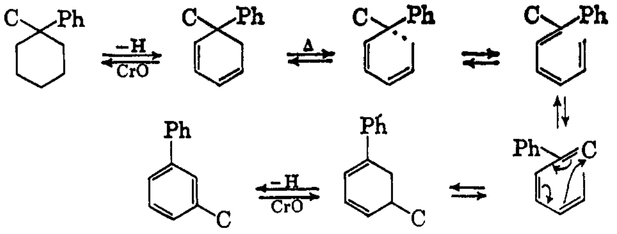


pansion has been observed in the conversion of Δ^2-cyclopentenylmethyl radicals into 4-cyclohexenyl radicals in solution.[11]

Diphenylmethane could also be formed by this expansion mechanism, but the absence of radioactivity from the nucleus of benzoic acid obtained from this hydrocarbon indicates that it must be formed solely by a direct 1,2-phenyl migration.

The second possible mechanism is the likely route for the insertion of most of the carbon-14 into the ring in *m*-phenyltoluene and involves ring opening with subsequent cyclization (Scheme II). Dehydrogenation

SCHEME II



on the catalyst is again suggested as the first step to yield a cyclohexadiene. A thermal homolytic fission in the gas phase could then yield a diradical stabilized as a diallyl system with additional stabilization by the phenyl group. The next step is merely a redistribution of the odd electrons to yield a stable triene system, which could undergo a facile double-bond isomerization to another triene. This could then cyclize to yield the *m*-phenyltoluene precursor. An analogous mechanism has been suggested to explain the products formed during thermal reactions of the *gem*-dimethyl type of conjugated cyclohexadienes[12] and of alkyl-1,3-cyclohexadienes.[13]

Since these mechanisms require the presence of the methyl group, they are not relevant to the reaction of 1,1-diphenylcyclohexane over chromia–alumina-B. Further, the added stability of the intermediate diradical from the phenyl group is important since *m*-xylene is not formed, for example, from 1,1-dimethylcyclohexane over this catalyst.

Biphenyl has a slight activity, which could arise by demethanation of the phenyltoluenes or their precursors. However, most of the biphenyl arises directly from the parent compound and the retention of radioactivity in the methyl group of toluene shows that it is also formed by direct fission of the 1-methyl-C^{14}-1-phenylcyclohexane.

The benzene had some activity, which may have arisen from fission of biphenyl, but in view of the low activity and high degree of dilution the calculated value of the carbon-14 content of the original benzene is not accurate.

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(10) L. H. Slaugh, E. F. Magoon, and V. P. Guinn, *J. Org. Chem.*, **28**, 2643 (1963).

(11) L. H. Slaugh, *J. Am. Chem. Soc.*, **87**, 1522 (1965).

(12) H. Pines and R. H. Kozlowski, *ibid.*, **78**, 3776 (1956).

(13) H. Pines and C. T. Chen, *ibid.*, **81**, 928 (1959).

Conclusion

During the dehydroisomerization of 1-methyl-1-phenylcyclohexane over chromia–alumina-B, intramolecular 1,2-, 1,3-, and 1,4-phenyl migrations occurred to yield *o*-, *m*-, and *p*-phenyltoluene, respectively, and the stability of possible intermediates showed that the migrations were one-step processes. 1,2-Phenyl migration also produced diphenylmethane.

However, carbon-14 tracer studies indicated that methyl insertion also occurred. Probable pathways are insertion by vinyl migration for all three phenyltoluenes and by ring opening with subsequent cyclization in the case of *m*-phenyltoluene and invoke established intermediates.

The phenyl migrations are consistent with the earlier postulation of radical species as intermediates over this catalyst and the formation of part of the *m*-phenyltoluene by this route appears to be the first example of a radical 1,3-phenyl migration.

Experimental Section

I. Apparatus and Procedure. 1. The Microreactor.—The pulse microreactor[14] was linked directly to a gas chromatograph. About 0.2 g of chromia–alumina-B was used and the charge of feedstock was about 2 μl of a mixture of 1-methyl-1-phenylcyclohexane (0.34309 g) and isodurene (0.02100 g). The isodurene was the internal standard and was stable under all the reaction conditions used.

The nongeminal methylphenylcyclohexanes and the phenyltoluenes were injected alone in 2-μl charges. Analyses of reaction products were performed on a 0.25 in. × 8.2 ft (2.5 m) 18% Carbowax 20M on 60–80 mesh Chromosorb P column, with a helium flow of 85.5 cc/min (10 cc/7 sec). The column temperature was programmed from 75 to 200° at 13°/min, beginning the programming 1.5 min after the injection of the reaction mixture into the reactor. Table VI shows the relative retention times under these conditions and the molar area responses. The *m*- and *p*-phenyltoluene were only partially resolved; so the areas of their peaks were calculated using the σ method.[15]

TABLE VI

RELATIVE RETENTION TIMES AND MOLAR AREA RESPONSES OF PRODUCTS FROM 1-METHYL-1-PHENYLCYCLOHEXANE

	Relative retn time	Molar area response
Benzene	0.27	1.565
Toluene	0.36	1.488
Isodurene[a]	0.65	1.000
1-Methyl-1-phenylcyclohexane	1.00	0.922
o-Phenyltoluene	1.39	0.897
Biphenyl	1.59	0.946
Diphenylmethane[b]	1.62	0.962
m-Phenyltoluene	2.01	0.972
p-Phenyltoluene	2.06	0.952

[a] Isodurene was used as an internal standard. [b] Values for diphenylmethane were included for completeness since they were formed in large-scale run.

2. Large-Scale Dehydroisomerization.—The apparatus and procedure for the dehydroisomerization of the 1-methyl-C^{14}-1-phenylcyclohexane was as described previously[9] except only one cut was taken.

The aromatic hydrocarbons were separated from the reaction product by means of an F & M Model 720 programmed-temperature gas chromatograph.[16] An initial separation was effected with a $^3/_8$ in. × 6.6 ft (2 m) preparative vpc column packed with 18% Carbowax 20M on 80–100 mesh Gas Pack W. The gas flow was 85.5 cc/min (10 cc/7 sec) and the temperature was programmed from 75 to 200° at 15°/min, beginning the programming 1.5 min after the injection of the reaction mixture. This gave benzene, toluene, and 2-phenyltoluene essentially pure as single fractions. Biphenyl and diphenylmethane were collected together as one fraction as were *m*- and *p*-phenyltoluene.

The *o*-phenyltoluene actually contained about 4% of biphenyl so this fraction was recycled under the conditions already described.

Biphenyl and diphenylmethane were separated on a $^3/_8$ in. × 16.4 ft (5 m) 12% silicon 550 on 30–60 mesh Chromosorb P column at 190° with a gas flow of 85.5 cc/min (10 cc/7 sec). The biphenyl was obtained pure, but the diphenylmethane was recycled to remove a small impurity of biphenyl.

The *m*- and *p*-phenyltoluenes were fractionated on a $^3/_8$ in. × 8.2 ft (2.5 m) 12% Apiezon-L and 8% Bentone 34 on 80–100 mesh Gas Pack W column at 190° with a gas flow of 85.5 cc/min (10 cc/7 sec). Only 10-μl injections of the mixture could be used and even then there was partial overlap so that three fractions had to be taken. Fraction 1 was *m*-phenyltoluene (98–99% pure), fraction 2 was a mixture, and fraction 3 was *p*-phenyltoluene (99% pure).

3. Oxidation of the Alkyl Aromatics. a. Toluene was oxidized to benzoic acid with hot alkaline potassium permanganate as described previously.[17] The crude acid was purified by sublimation at 110–120° and then recrystallized from hot water, mp 119–120° (lit.[18] mp 122.4°).

b. Diphenylmethane was oxidized to benzoic acid in small portions (0.5 g) in a neutral solution of potassium permanganate (4 g) in water (60 ml), stirring at 85–90° for 24 hr. Excess potassium permanganate was precipitated as manganese dioxide, which was filtered off by adding methanol. The filtrate was made alkaline and unchanged diphenylmethane was extracted with ether. Acidification of the filtrate allowed extraction of the benzoic acid, which was purified as above, mp 117–119°.

c. *o*-Phenyltoluene.—A mixture of *o*-phenyltoluene (0.5 g) and N-bromosuccinimide (1 g) in dry carbon tetrachloride (20 ml) containing a pinch of dibenzoyl peroxide was heated at 90° for 2.5 hr. The succinimide was filtered off and removal of the solvent yielded crude 2-phenylbenzyl bromide, which was treated with a solution of potassium permanganate (2.2 g) in water (100 ml) at 85° for 11 hr. The reaction mixture was worked up as before utilizing an alkaline filtrate first to extract unchanged 2-phenylbenzyl bromide, which was recycled. Acidification of the filtrate allowed extraction of 2-phenylbenzoic acid, which contained a small amount of benzoic acid. This impurity was removed by fractional sublimation under high vacuum. The benzoic acid (17%) was essentially removed after 2 hr at 105–110°. The 2-phenylbenzoic acid (49%) sublimed in the subsequent 6–8 hr at 110–120°, mp 108–110° (lit.[19] mp 110–111°).

d. *m*-Phenyltoluene was oxidized to 3-phenylbenzoic acid, which initially contained some benzoic acid and isophthalic acid, *via* 3-phenylbenzyl bromide by the procedure described for *o*-phenyltoluene. Again the acid was purified by fractional sublimation under high vacuum. The benzoic acid (13%) sublimed in 2 hr at 105–110°, followed by an intermediate fraction (17%) of impure product obtained in 1 hr at 145–150°, and then the 3-phenylbenzoic acid (47%) sublimed in an additional 2 hr at 145–150°, mp 161–163° (lit.[20] mp 160–161°). A residue of isophthalic acid remained in the apparatus.

e. *p*-Phenyltoluene.—A mixture of *p*-phenyltoluene (0.5 g), glacial acetic acid (55 ml), and a 1:1 mixture (20 ml) of Jones reagent[21] and water was stirred at room temperature for 8 hr. It was then poured into water (300 ml) when the 4-phenylbenzoic acid precipitated. This was filtered off, washed well with water, and then dried in a vacuum desiccator before being sublimed at 205° under high vacuum, followed by recrystallization from aqueous ethanol. The pure 4-phenylbenzoic acid (45%) had mp 218–220° (lit.[22] mp 218–219°).

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(14) P. Steingaszner and H. Pines, *J. Catalysis*, **5**, 356 (1966).

(15) J. C. Bartlett and D. M. Smith, *Can. J. Chem.*, **38**, 2057 (1960).

(16) F & M Scientific Corp., Avondale, Pa.

(17) H. Pines, C. T. Goetschel, and S. M. Csicsery, *J. Org. Chem.*, **28**, 2713 (1963).

(18) J. Timmermans and F. Burriel, *Chim. Ind.* (Paris), **25**, 196 (1931).

(19) R. Fittig and E. Ostermeyer, *Ann.*, **166**, 374 (1873).

(20) M. Gomberg and J. C. Pevnet, *J. Am. Chem. Soc.*, **48**, 1380 (1926).

(21) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

(22) O. Dobner, *Ann.*, **172**, 111 (1874).

4. **Decarboxylation.**—All the aromatic carboxylic acids were decarboxylated according to the procedure of Calvin, *et al.*[23] The benzene obtained from benzoic acid distilled from the reaction mixture and was collected in a trap. However, biphenyl was produced from the phenylbenzoic acids and remained in the reaction mixture. Therefore, the contents of the decarboxylation tube were filtered through a pad of diatomaceous earth and the tube was washed out well with water and ether, which was used to wash the filtration pad. The filtrate was then acidified with concentrated hydrochloric acid and then extracted with three portions of ether. The combined etheral extracts were washed with water and dried over anhydrous sodium sulfate. Removal of the ether yielded crude biphenyl, which was purified by preparative vpc of an etheral solution on the Carbowax column used initially (section I-2) at 200° with a gas flow of 85.5 cc/min (10 cc/7 sec). The melting point was always within 2° of literature and yields for all products of decarboxylation were between 50 and 90%.

5. **Radiochemical Assay.**—All samples were assayed by first converting them into gaseous carbon dioxide. The organic samples were burned by wet combustion according to the procedure of Van Slyke, *et al.*[24] Carbon dioxide was liberated from barium carbonate by hot sulfuric acid.

The radioactivity assay was performed in a 250-ml D.C.-type 302 stainless steel ionization chamber connected to a vibrating reed Dynacon electrometer, Model 600, made by Nuclear-Chicago Corp. Each sample was assayed both by the steady state and by the rate of change methods. At least two assays were made for each sample.

II. **Chemicals.** 1. **Benzene, toluene, biphenyl, diphenylmethane, and *m*- and *p*-phenyltoluenes** were provided by commercial sources; the last four compounds were purified before use.

2. **1-Methyl-1-phenylcyclohexane.**—The inactive compound was prepared essentially by the procedure of Ipatieff, *et al.*[25]

Hydrogenation of *o*-cresol (400 g) in absolute ethanol (200 ml) using nickel–kieselguhr (20 g) at 160–170° and 100 atm yielded 2-methylcyclohexanol (84%), bp 48–50° (5 mm). Dehydration over alumina at 410–420° at hourly liquid space velocity 0.6–0.9 gave a 93% yield of olefin mixture. A solution of this olefinic product (0.5 mole) in benzene (0.75 mole) was added to a mixture of benzene (0.75 mole) and hydrogen fluoride (50 g) cooled at 0° to yield 1-methyl-1-phenylcyclohexane (51%), bp 106–107° (9 mm) (lit.[26] bp 118° (12 mm)).

3. **1-Methyl-2-phenylcyclohexane** was prepared by the procedure of Goodman and Wise.[27] Interaction of phenylmagnesium bromide (0.5 mole) and 2-methylcyclohexanone (0.38 mole) yielded 2-methyl-1-phenylcyclohexanol (68%). Dehydration of this alcohol over alumina gave an olefinic mixture (83%), which was hydrogenated using 5% palladium–carbon to yield 1-methyl-2-phenylcyclohexane (80%).

4. **1-Methyl-3-phenylcyclohexane.**—An analytical sample was prepared by an analogous interaction of phenylmagnesium bromide and 3-methylcyclohexanone. Dehydration was accomplished by mixing the alcohol with toluene and powdered potassium bisulfate and heating to boiling to remove the water as an azeotrope with toluene. The crude olefin was hydrogenated at atmospheric pressure using platinum oxide.

5. **1-Methyl-4-phenylcyclohexane.**—An exactly analogous procedure to that used for the 3 isomer was followed utilizing 4-methylcyclohexanone.

6. ***o*-Phenyltoluene** was obtained by dehydrogenation of 1-methyl-2-phenylcyclohexane by heating under reflux (250°) with 10% palladium–carbon in nitrogen for 138 hr.

7. **1-Methyl-C^{14}-1-phenylcyclohexane.** a. **1-Methyl-C^{14}-cyclohexanol.**—A solution of methyl-C^{14} iodide (12.4 g, 0.086 mole, 10 μCi of C^{14}) in dry ether (100 ml) was added dropwise to a vigorously stirred mixture of magnesium turnings (2.2 g, 0.09 g-atom) and dry ether (40 ml), which was cooled externally with an ice bath. The addition took 30 min, after which a solution of cyclohexanone (10.4 g, 1.06 moles) in dry ether (40 ml) was added dropwise over 30 min to the cooled Grignard solution. Stirring was continued for a further 30 min when a solution of ammonium chloride (18 g) in water (80 ml) was added slowly. The etheral layer was separated off and combined with etheral extracts of the aqueous layer. Removal of the ether from the dried (Na_2SO_4) solution gave crude 1-methyl-C^{14}-cyclohexanol.

b. **1-Methyl-C^{14}-phenylcyclohexane.**—Benzene (25 g, 0.32 mole) was added dropwise over 10 min to anhydrous hydrogen fluoride (25 g, 1.25 moles), which was cooled externally in an ice bath. To this a solution of the crude 1-methyl-C^{14}-cyclohexanol in benzene (25 g, 1.25 moles) was added dropwise with continued cooling. The reaction mixture was then stirred for 5 min after which the excess hydrogen fluoride was neutralized with sodium bicarbonate. Ice was added periodically for cooling. The organic layer was then separated off, combined with ethereal extracts of the aqueous layer, and dried over anhydrous sodium sulfate. Excess solvent was removed at 160 mm on an oil bath at 45–56°. Then inactive 1-methyl-1-phenylcyclohexane (9 ml) was added and 13.3 g of product was distilled off at 130–135° (4.0 mm). A further portion (4 ml) of inactive hydrocarbon was added and 7.3 g of product was distilled at 128° (33 mm). A final portion (3 ml) of inactive 1-methyl-1-phenylcyclohexane was added and a fraction of 2.6 g was taken over a wide temperature range until no more product distilled over. This procedure was employed for maximum recovery of carbon-14.

After preliminary assays of radioactivity, fractions 1 and 2 were combined yielding a final product with an activity of 40.7 μCi/mmole and greater than 99% purity. This represented a 48% recovery of carbon-14.

Catalyst.—The alumina-B was prepared as described previously[6] and graded (12–16 mesh) before being impregnated with chromia.[6]

Registry No.—1-Methyl-1-phenylcyclohexane, 828-45-5; 1-methyl-C^{14}-1-phenylcyclohexane, 15297-40-2.

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