combined wt 0.6 g. After recrystallization, this material [(−)-(*SS*)-VI] from ether–pentane gave mp 133–134°. *Anal.* Found: C, 69.68; H, 6.93.

N-(α-**Phenylethyl**) **Methylphenylphosphinic Amide** [(−)-(*SS*)-VI] **from Menthyl or Cholesteryl Methylphenylphosphinates** [(−)-(*S*)-II **and** (−)-(*S*)-I].—The procedure is illustrated as applied to the cholesteryl ester (−)-(*S*)-I. To a solution (4.12 g or 34 mmol) of (−)-(*S*)-α-phenylethylamine, $[\alpha]^{25}D$ −40.1° (neat),[8] in 20 ml of dry benzene was added 21.3 ml of a 1.6 *M* solution of *n*-butyllithium (34 mmol) in hexane with stirring under dry nitrogen. The mixture was stirred at reflux for 1 hr. A solution of 0.92 g (1.7 mmol) of (−)-(*S*)-I, $[\alpha]^{25}D$ −81.4°, *c* 4.53, chloroform (or 1.7 mmol of (−)-(*S*)-II, $[\alpha]^{25}D$ −94°, *c* 1.45, benzene) in 20 ml of dry benzene was added with stirring, and the mixture was held at reflux for 5 hr. The reaction mixture was shaken with 10% hydrochloric acid and dichloromethane. The organic layer was washed, dried, and evaporated to give 0.97 g of residue which was chromatographed on 25 g of silica gel. The first 4 fractions (75 ml each) were eluted with 1:1 ether–acetone, fractions 5–8 with pure acetone. The yellow oil from 5 and 6 was crystallized (nonfractionally) from ether–pentane to give 0.11 g (25%) of (−)-(*SS*)-VI, $[\alpha]^{25}D$ −63° (*c* 1.55, chloroform), mp 132–133.5°. An identical yield, melting point, and rotation were obtained from (−)-(*S*)-II. Examination of the crude amides from both preparations of (−)-(*SS*)-VI with tlc on silica gel plate, acetone–methanol, 9:1, showed the absence of other diastereomers. Control experiments with both diastereomers demonstrated that as little as 1–2% could have been detected.

N-**Phenyl Methylphenylphosphinic Amide** [(−)-(*S*)-III].—Application of the above procedure to lithium anilide (10 mol excess) and either cholesteryl or menthyl methylphenylphosphinate [(−)-(*S*)-I or (−)-(*S*)-II] gave (−)-(*S*)-III. The yield after chromatography and nonfractional crystallization of (−)-(*S*)-III (acetone–pentane) from (−)-(*S*)-I was 35%, mp 161–163°, $[\alpha]^{25}D$ −26.2° (*c* 1.33, methanol). The yield after chromatography and nonfractional crystallization (acetone–pentane) from (−)-(*S*)-II was 38%, mp 161–163°, $[\alpha]^{25}D$ −26.1° (*c* 0.83, methanol). The literature[4] reported mp 164°, $[\alpha]^{25}D$ −25.8° (c 0.76, methanol).

o-**Dodecyloxybromobenzene**.—A mixture of *o*-bromophenol (82.5 g), 250 ml of 95% ethanol, and 21 g of sodium hydroxide pellets was heated into solution, and 113.2 g of dodecyl bromide was added. After 24 hr at reflux, the product was isolated by extraction and distillation, wt 142 g (92%), bp 153° (0.14 mm). *Anal.* Calcd for $C_{18}H_{29}BrO$: C, 63.34; H, 8.56. Found: C, 63.47; H, 8.54.

o-**Dodecyloxyphenylmethylphenylphosphine Oxide** (VII).—The Grignard reagent of *o*-dodecyloxybromobenzene was prepared by the "entrainment method"[12] from 34.1 g of bromide and 2.6 g of magnesium in 500 ml of dry ether. To this stirred mixture under nitrogen was added dropwise 17.4 g of methylphenylphosphinic chloride[10] in 200 ml of dry ether. The resulting viscous mixture was shaken with dilute hydrochloric acid, and the organic phase was washed with water, dried, evaporated, and distilled to give 19.6 g (49%) of VII as a viscous and slowly crystallizing oil, bp 188° (0.14 mm). *Anal.* Calcd for $C_{25}H_{37}O_2P$: C, 74.97; H, 9.31. Found: C, 75.01; H, 9.29.

Attempted Resolution by Glc.—A 0.25 in. (i.d.) × 10 ft column was packed with a 10% mixture by weight of diastereomerically pure cholesteryl methylphenylphosphinate [(−)-(*S*)-I] on Chromosorb W (80–100 mesh). About 15 g of mixture filled the column, which was cured in an oven at 170° for 90 min and at 155° for 3 hr. A small sample of pure (−)-(*S*)-I was found not to change its rotation when held at 165° for 12 hr. The chromatographic experiments were carried out on a Perkin-Elmer vapor fractometer, Model 154, at a column temperature of 144° with helium as a carrier. On this column, the following racemates had the indicated retention times, and the peaks were sharp: 2-octanol, 14 min; 2-phenylpropionitrile, 32 min; 3-methoxy-3-phenyl-2-butanone, 34 min; 2-methyl-1-phenyl-1-propanol, 28 min; 3-methoxy-2-methyl-3-phenyl-2-butanol, 44 min. In experiments that involved *o*-dodecyloxyphenylmethylphenylphosphine oxide (VII), 5% by weight of VII on Chromosorb W was employed in the same type of column and in the same machine and carrier gas. At 85°, 1-butanol, 2-butanol, and *tert*-butyl alcohol gave 6.3, 2.9, and 1.3 min retention times, respectively. At 105°, 1-octanol and 2-octanol gave 14.7 and 4.7 min retention time, respectively. At 87°, 1-butanol, 2-butanol, and 2-pentanol gave 2.7, 1.5, and 2.4 min retention times, respectively.

Registry No.—(−)-(*S*)-I, 20752-41-4; (−)-(*S*)-II, 16934-93-3; (−)-(*R*)-II, 26963-82-6; (−)-(*SR*)-VI, 20752-44-7; (−)-(*SS*)-VI, 20752-43-6; VII, 26910-10-1; *o*-dodecyloxybromobenzene, 26910-11-2.

(12) D. E. Pearson, D. Cowan, and J. D. Beckler, *J. Org. Chem.*, **24**, 504 (1959).

Carbon-14 Tracer Study of the Dehydrocyclization of *n*-Heptane

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Received May 12, 1970

The ^{14}C distribution in toluene from the dehydrocyclization of *n*-heptane-1-^{14}C and -4-^{14}C, both over the same chromia on "nonacidic" alumina preparation, is consistent with 80% or more of the aromatic being formed by direct six-carbon ring formation. Thus, chromia on "nonacidic" alumina can give results similar to other chromia and chromia–alumina. In general, a dehydrocyclization mechanism involving various size intermediates is not necessary even for the "nonacidic" catalyst.

The mechanism for the heterogeneous catalytic conversion of paraffins to aromatics, dehydrocyclization, has been widely studied.[1] Early workers, guided by aromatic product distributions and kinetics, supported a dehydrocyclization mechanism involving direct six-carbon ring formation. An early ^{14}C tracer study[2] also supported this mechanism.

Results of more recent ^{14}C tracer studies[3,4] were incompatible with this mechanism. To explain their ^{14}C distributions, Pines and Chen[4] proposed that cyclization to both six- and seven-membered-ring intermediates participate in the mechanism. The contribution of these intermediates varied with time on stream and catalyst. Such competition between various size ring intermediates would not allow the dehydrocyclization mechanism to have predictive value. On the other hand, Feighan and Davis[5] found that *n*-heptane-4-^{14}C

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(1) For a review of the literature, see (a) A. H. Steiner in "Catalysis," Vol. 4, P. H. Emmett, Ed., Reinhold, New York, N. Y., 1957, p 529; (b) H. Hansch, *Chem. Rev.*, **52**, 353 (1953); (c) H. Pines and C. T. Goetschel, *J. Org. Chem.*, **30**, 3530 (1965).

(2) R. W. Wheatcroft, Dissertation, University of California, 1949.

(3) J. J. Mitchell, *J. Amer. Chem. Soc.*, **80**, 5848 (1958).

(4) H. Pines and C. T. Chen, *J. Org. Chem.*, **26**, 1057 (1961).

(5) J. A. Feighan and B. H. Davis, *J. Catal.*, **4**, 594 (1965).

over a similar chromia–alumina catalyst gave a product with a tracer distribution consistent with direct six-carbon ring formation.

Contradictory results from different laboratories often are a result of the difficulty in preparing reproducible heterogeneous catalysts. We now report a study of the dehydrocyclization of *both* *n*-heptane-1-^{14}C and -4-^{14}C over the *same* preparation of chromia on "nonacidic" alumina in order to further clarify the mechanistic picture in this complex system.

Results and Discussion

The results for the dehydrocyclization of the two ^{14}C-labeled heptanes over the same chromia catalyst supported on "nonacidic" alumina at 500° are shown in Table I. The precentage of ^{14}C label in the methyl

TABLE I

METHYL ACTIVITY IN TOLUENE FROM DEHYDROCYCLIZATION OF *n*-HEPTANE-1-^{14}C AND *n*-HEPTANE-4-^{14}C

Sample	Time on stream, min	Liquid collected, cc	Conversion to toluene, mol % in liquid product	% methyl label of toluene
		n-Heptane-1-^{14}C		
1	45	0.4	49	43
2	97	1.0	41	39
3	137	0.8	37	40
		n-Heptane-4-^{14}C		
1	45	0.4	46	2.6
2	105	1.2	44	2.8
3	160	1.1	43	2.7
4	215	1.0	43	3.0

group of toluene is about 40% for *n*-heptane-1-^{14}C. The three samples collected at different time on stream show no variation in the label distribution. This is in contrast to the results of Pines and Chen[4] who found that the methyl-labeled toluene increased in the samples collected at increasing time on stream.

The first liquid sample in the present *n*-heptane-1-^{14}C run (0.4 ml, using 5 ml of catalyst) should correspond, at least qualitatively, to the first sample collected by Pines and Chen,[4] since it was taken at an earlier time on stream. (The first sample of Pines and Chen[4] calculates to be about 0.7 ml for 5 ml of catalyst.) Therefore, the difference in the amount of methyl label for the first sample of toluene from *n*-heptane-1-^{14}C for the present study and Pines and Chen[4] cannot be attributed to catalyst changes with time on stream.

The methyl label for toluene obtained from *n*-heptane-4-^{14}C is significantly higher than expected for only direct six-carbon ring formation (2.5–3.0% *vs.* predicted 0.0%). This methyl label is slightly greater than obtained by Feighan and Davis[5] in their study using *n*-heptane-4-^{14}C over chromia on "nonacidic" alumina (1.0–1.6% methyl label). Even so, the methyl activity is still much lower than would be expected for the nearly isotopic equivalency found by Pines and Chen[4] (and perhaps Mitchell[3]).

Mitchell[3] obtained toluene with about 25% ^{14}C in the methyl position from the dehydrocyclization of *n*-heptane-1-^{14}C over a chromia–alumina catalyst promoted with potassium and cerium ("nonacidic" catalyst). He proposed three reaction pathways which could explain the low methyl-labeled toluene: (a) the formation of a cycloheptane intermediate, (b) the formation of a bicycloheptene intermediate followed by opening of one ring to yield toluene, and (c) reversible isomerization between C_5- and C_6-ring structures.

Pines and Chen[4] found the predicted 50% methyl label in toluene from the dehydrocyclization of *n*-heptane-1-^{14}C over unsupported chromia and 40% methyl label in toluene using chromia supported on "acidic" alumina. But dehydrocyclization using chromia supported on "nonacidic" alumina initially yielded toluene with 17.5% (or less) ^{14}C in the methyl position; at later times on stream the methyl ^{14}C content has increased to 32%. An adsorbed cycloheptane intermediate that was able to "roll around" on the surface was proposed to give carbon equivalency at all positions; the adsorbed cycloheptane then underwent ring contraction to form a C_6 ring. Pines and Goetschel[1c] have obtained results for several reactants in addition to *n*-heptane that show that their chromia on "nonacidic" alumina gave much different results than either chromia or chromia on "acidic" alumina.

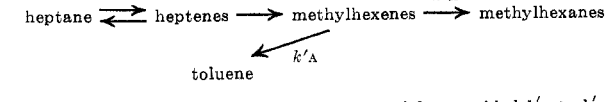
Feighan and Davis[5] obtained results with *n*-heptane-4-^{14}C which were in satisfactory agreement with C_6-ring formation. Contrary to Pines and Chen, a larger amount of isotope scrambling in the toluene was obtained over unsupported chromia than over chromia supported on either "acidic" or "nonacidic" alumina. For all three catalysts, the toluene product was predominately labeled at the position predicted for direct C_6-ring formation, the ring position meta to the methyl substituent.

The reason for the significant difference between results which support direct C_6-ring formation (this study, ref 2 and 5) and those in disagreement with this cyclization pathway[3,4] is not apparent. It is possible that the amount or location of the potassium "promotor" used to make the alumina "nonacidic" plays a more important role than previously suspected. Small differences in catalyst pretreatment may also cause large differences in the catalytic properties of potassium promoted catalysts. The amount of chromia on the support may be responsible for the different results.

This study cannot provide an answer to the mechanism responsible for the ^{14}C label at positions other than those predicted by direct C_6-ring formation. It is conceivable that this ^{14}C scrambling could occur through a cycloheptane intermediate. However, it is also possible to explain the ^{14}C scrambling by isomerization to a methylhexane carbon skeleton prior to or during cyclization.[6]

Only Feighan and Davis[5] have determined the ^{14}C ring distribution in toluene obtained from *n*-heptane dehydrocyclization. For *n*-heptane-4-^{14}C, the ^{14}C was

(6) Methylhexanes were not present in the liquid product in significant quantities. There are many isomerization mechanisms that could lead to methylhexanes. One such pathway involves an olefin intermediate. The



absence of methylhexanes can then be accounted for provided $k'_A > k'_H$ or by preferential conversion of methylhexanes. Our unpublished results show that both heptane and methylhexanes are converted at about the same rate when passed over the catalyst under similar conditions. It is known that olefins are aromatized more readily than paraffins,[1] but little is known about the relative rates k'_A and k'_H.

about equally distributed in all positions except the ring position meta to the methyl group. If we assume a similar ^{14}C distribution for the toluene obtained from *n*-heptane-4-^{14}C in the present study (*i.e.*, the ring positions, excluding the position meta to the methyl group, have the same activity as experimentally determined for the methyl position), we calculate that about 80% of the ^{14}C is in the position meta to the methyl group. For toluene from *n*-heptane-1-^{14}C, the methyl label was about 40%, also about 80% of that predicted by a direct C_6-ring formation mechanism.

The results of this study with *n*-heptane-4-^{14}C substantiate the earlier results of Feighan and Davis;[5] both support direct C_6-ring formation. Our tracer results suggest that the same amount of direct C_6-ring formation occurs over "nonacidic" chromia–alumina for *n*-heptane labeled either in the 1 or 4 position. More important, the results of the present study and those of Feighan and Davis[5] support a heptane dehydrocyclization mechanism of direct C_6-ring formation over a "nonacidic" chromia–alumina catalyst as well as over other chromia catalysts.

Experimental Section

Catalyst.—The "nonacidic" alumina was prepared by precipitation from potassium aluminate with CO_2.[7] The alumina was washed so that the potassium content was 0.1 wt % (based on weight after 600° calcination). The alumina was impregnated with chromic acid; the final catalyst contained 10.6 wt % Cr (15.6 wt % Cr_2O_3).

Hydrocarbons.—*n*-Heptane-4-^{14}C was prepared as shown in synthetic Scheme I.[8]

SCHEME I

$$HC^*O_2H \xrightarrow{EtOH} HC^*O_2C_2H_5 \xrightarrow{PrMgBr} C_3H_7C^*HOHC_3H_7$$

$$C_3H_7C^*HOHC_3H_7 \xrightarrow{HOAc} C_3H_7CHC_3H_7 \xrightarrow{400°}$$
(OAc)

$$C_3H_7C^*H{=}CHC_2H_5$$

$$C_3H_7C^*H{=}CHC_2H_5 \xrightarrow[H_2]{PtO_2} C_3H_7C^*H_2C_3H_7$$

n-Heptane-1-^{14}C was prepared as shown in synthetic Scheme II. Sodium formate was purchased from Tracerlab. Sodium *n*-heptanoate-1-^{14}C was purchased from Nuclear-Chicago Corp.

Procedure.—The catalyst (5 ml, 4 g) was placed in an electrically heated Vycor glass continuous-flow unit and reduction

(7) H. Pines and C. T. Chen, *J. Amer. Chem. Soc.*, **82**, 3562 (1960).
(8) R. E. McMahon, *Ind. Eng. Chem.*, **47**, 844 (1955).

SCHEME II

$$C_6H_{13}C^*O_2H \xrightarrow{LiAlH_4} C_6H_{13}C^*H_2OH \xrightarrow{PBr_3} C_6H_{13}C^*H_2Br$$

$$C_6H_{13}C^*H_2Br \xrightarrow{Mg} C_6H_{13}C^*H_2MgBr \xrightarrow{H_2O} C_6H_{13}C^*H_3$$

effected *in situ* in flowing hydrogen (4 ml/min) for 3 hr. The labeled reactant was introduced by a motor-driven syringe pump (LHSV 0.3). Runs were effected at 500° and 1 atm. A detailed description of the apparatus has been reported earlier.[9]

The liquid products were diluted to about 10-cc volume with a 50:50 volume mixture of unlabeled *n*-heptane–toluene. This mixture was separated on a silica gel column using isopropyl alcohol as eluting agent. The first 0.5 ml of the toluene fraction eluting from the column was discarded.

The toluene was oxidized to benzoic acid using alkaline potassium permanganate. Details of the method are given in ref 5. The benzoic acid was burned to CO_2 by the van Slyke procedure and the CO_2, trapped in NaOH, was then collected as barium carbonate. The decarboxylation of benzoic acid was accomplished by heating at 260° in a CuO–quinoline mixture. Two, and for about half of the cuts three, combustions and decarboxylations were done on the benzoic acid. The percentages in the tables were calculated using an average of the $BaCO_3$ counts. Representative activities for the determinations are given in Table II.

TABLE II
REPRESENTATIVE DATA SHOWING THE REPRODUCIBILITY OF THE DECARBOXYLATION, BENZOIC ACID OXIDATION, AND $BaCO_3$ COUNTING PROCEDURES

	$BaCO_3$ sample[a]	Activity, counts/(min 100 mg of $BaCO_3$)
Sample 1, methyl carbon	1	16,719
(*n*-heptane-1-^{14}C run)	2	14,193
	3	14,178
Sample 1, benzoic acid carbons	1	4,733[b]
(*n*-heptane-1-^{14}C run)	2	5,191

[a] Three portions of the benzoic acid (from toluene oxidation) were decarboxylated; two portions of the benzoic acid were oxidized. [b] The activity for $BaCO_3$ from the total benzoic acid sample is less than that from methyl decarboxylations because the ^{14}C is diluted by six inactive carbons in the benzoic acid.

The ^{14}C activity of the $BaCO_3$ samples was determined by liquid scintillation. The sample was suspended in the scintillation solution (5 g of PPO and 0.3 g of POPOP per liter of toluene containing 4 wt % Cab-o-Sil).

Registry No.—*n*-Heptane-1-^{14}C, 26960-94-1; *n*-heptane-4-^{14}C, 26960-95-2.

Acknowledgment.—We are grateful to Dr. H. Sherry and Mr. C. Adams of Mobil Research and Development Corporation for performing the ^{14}C activity determination.

(9) B. H. Davis and P. B. Venuto, *J. Catal.*, **15**, 363 (1969).