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Catalytic Reactions of *n*-Pentylbenzene and 2-Phenylpentane

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n-Pentylbenzene and 2-phenylpentane were reacted over a series of catalysts covering a wide range of acidic and dehydrogenation activities.

Acid-catalyzed cyclization favors the formation of six-membered rings provided that the same type of carbonium ion intermediate is involved in both six- and five-membered cyclization processes. Side-chain branching increases the rate of acid-catalyzed cyclization. Dehydrogenation of the alkylbenzene could be the rate-controlling step in acid-catalyzed cyclizations.

Pt-catalyzed cyclization of *n*-alkylbenzenes forms about equal amounts of five- and six-membered rings. Five-membered ring cyclization is favored with secondary alkylbenzenes. The Pt does not function as an acid when catalyzing cyclization of alkylbenzenes.

Isomerization may be catalyzed by acids or by the Pt metal. Pt-catalyzed isomerizations proceed either via cyclic intermediates or through 1,3-diadsorbed intermediates. In certain Pt-catalyzed isomerizations, a 1,4-diadsorbed intermediate might also be involved.

At 371°C, acid-catalyzed cracking rates of a secondary side chain are about an order of magnitude higher than that of a normal side chain. Pt-catalyzed hydrogenolysis affects the side-chain bonds of *n*-alkylbenzenes at an approximately equal rate. In secondary alkylbenzenes, cleavage of the bond between the tertiary carbon atom and the ring is preferred.

This work completely confirmed the reaction mechanisms suggested by our earlier *n*-butylbenzene work; namely, (a) in addition to its dehydrogenation activity, Pt has considerable cyclization, isomerization, and hydrogenolysis activities; (b) cyclization occurs on both acid and metal sites; and (c) in the acid-catalyzed cyclization process, the stability of the carbonium ion intermediate determines whether cyclization forms five- or six-membered ring products.

Dehydrogenation of cyclohexane derivatives, dehydroisomerization of alkylcyclopentanes, dehydrocyclization of paraffins, isomerization, and cracking are the most important reactions taking part in the catalytic reforming process. Dual-functioning catalysts—having acidic and dehydrogenation components—are used. The roles of acidic and metallic components in these catalysts were recently clarified using *n*-butylbenzene as a model compound (*1*). Results on two methyl homologs of *n*-butylbenzene (*n*-pentylbenzene and 2-phenylpentane) are reported here.

EXPERIMENTAL

Hydrocarbon Feeds

n-Pentylbenzene was purchased from Matheson Coleman and Bell Company. Its purity (by gas chromatography) was 99.8%. 2-Phenylpentane was purchased from the Chemical Samples Company (Columbus, Ohio). Its purity was 99.26%.

Catalysts and Procedure

Preparation and physical properties of platinum (2%) on silica gel, platinum (2%) on silica-alumina, platinum (0.85%)

TABLE 1

Reactions of *n*-Pentylbenzene over Different Catalysts[a]

Catalyst[b]		Chromia-Alumina-Potassia		Platinum (2%) on Silica Gel				Pt (0.75%) on Alumina	Platinum (2%) on Silica-Alumina			Silica-Alumina
Experiment Number		1	2	3	4	5	6	7	8	9	10	11
Reaction Temperature, °C		371	427	371	371	427	482	371	371	427	482	427
Liquid Hourly Space Velocity		13.2	6.8	13.2	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8
Residence Time, Seconds		0.2	0.40	0.22	0.43	0.40	0.37	0.43	0.43	0.40	0.37	0.40
Product Composition, Moles Per 100 Moles of Feed[c]	Relative GC Retention Time[d]											
Unreacted *n*-Pentylbenzene	17.2	99.28	95.34	96.11	89.54	77.06	64.19	89.29	55.66	35.34	39.13	94.15
Benzene	0.46	0.04	0.09	0.20	0.36	0.43	1.10	0.92	0.64	1.07	3.42	4.00
Toluene	1.00	0.03	0.05	0.16	0.26	0.38	0.93	0.42	0.08	0.25	0.45	0.06
Ethylbenzene	1.97	0.01	0.04	0.15	0.28	0.68	1.44	0.56	0.10	0.35	0.75	0.10
Styrene	3.18				0.01	0.01	0.12				0.08	
o-Xylene	2.7					0.01	0.06		0.01	0.01	0.03	0.01
n-Propylbenzene	3.78	0.006	0.01	0.10	0.20	0.33	0.62	0.18	0.02	0.10	0.16	0.01
Cumene	3.0					0.03	0.15	0.01				
Methylstyrenes	4.88				0.02	0.06	0.10					
Indan	8.05			0.03	0.11	0.25	0.40	0.04	0.03	0.14	0.21	
n-Butylbenzene	8.1		0.02	0.12	0.25	0.34	0.78	0.20	0.03	0.08	0.08	0.006
Isobutylbenzene	5.25					0.01	0.01					
sec-Butylbenzene	5.28				0.01	0.04	0.06					
1-Methylindan	11.0			0.05	0.17	0.39	0.45	0.13	0.04	0.18	0.22	0.02
1-Methylindene	22.8				0.02	0.14	0.47	0.02		0.08	0.19	
Naphthalene	36.0				0.06	0.23	0.90	0.03	0.10	0.32	0.58	
2-Phenylpentane	10.6			0.09	0.18	0.63	0.61	0.11	0.10	0.18	0.10	0.03
3-Phenylpentane	8.95			0.08	0.16	0.21	0.26	0.06	0.06	0.07	0.07	0.02
1-Phenyl-2-Methylbutane	11.80			0.02	0.06	0.07	0.10	0.03	0.08	0.10	0.04	0.09
1-Phenyl-3-Methylbutane	12.00	0.01	0.02	0.08	0.10	0.11	0.12	0.05	0.17	0.20	0.06	0.06
2-Phenyl-3-Methylbutane	8.84			Trace	0.04	Trace	0.05	0.03	0.01			
1-Phenylpentenes		0.58	3.77	0.59	0.59	2.85	8.96	0.55	0.27	0.60	0.98	0.03

2-Phenyl-*cis*-2-Pentene	27.3					0.04	0.11	0.03				
1-Ethylindan	23.5		0.07	1.15	3.80	5.33	2.45	3.22	1.32	1.25	0.71	0.33
1-Ethylindene	46.0			0.10	0.30	1.52	2.54	0.18	0.05	0.25	0.27	
Dimethylindan[e]		0.04	0.55	0.36	1.10	2.46	2.26	0.89	3.08	6.40	7.42	0.80
Dimethylindene[f]				0.05	0.15	0.86	3.16	0.11	0.09	0.55	1.07	0.01
Other Aromatic Compounds[g]				0.01	0.28	0.60	1.36	0.12	0.04	0.42	0.39	0.13
1-Methylnaphthalene	87.6		0.04	0.54	1.91	4.43	6.10	2.70	27.71	29.42	17.48	0.05
2-Methylnaphthalene	76.6			0.01	0.04	0.10	0.20	0.12	10.11	21.54	24.51	0.09
C_{12} and Higher Aromatics						0.40			0.20	1.10	1.60	
Methane			0.03		0.25	0.97	3.40	0.38	0.06	0.70	1.34	0.01
Ethane, Ethylene		0.007	0.01		0.12	0.46	1.09	0.17	0.02	0.24	1.04	0.09
Propane, Propylene		0.01	0.03		0.17	0.45	0.81	0.50	0.06	0.33	0.95	0.10
Butanes, Butenes		0.04	0.03		0.19	0.35	0.57	0.36	0.02	0.25	0.16	0.22
Pentanes		0.01	0.05		0.26	0.36	0.37	0.61	0.26	0.55	1.57	1.60
Pentenes						0.03	0.14		0.11	0.07	0.60	2.20
Other Aliphatics						0.05	0.11	0.01				

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[a] Reaction conditions: Atmospheric total pressure, an initial hydrogen-to-feed ratio of 3.0, and an initial hydrocarbon partial pressure of 0.25 atm. In Experiments 1 and 3 the feed flow rate was 6.6 ml/hour, and the H_2 flow rate (measured at 25°C and 1 atm) was 46.8 ml/minute. In all the other experiments feed flow rates were 3.42 ml/hour, and H_2 flow rates were 24.3 ml/minute. Experiments 1 and 3 were 20 minutes long. All other experiments were 30 minutes long. Reaction effluent samples were taken at 20 minutes onstream times (15 minutes in Experiments 1 and 3). Liquid products were collected from the fifth to the last minute of each experiment. The feed was 99.8% pure (by gas chromatography).

[b] We used 0.5 ml 60 to 100 mesh size catalyst in each experiment. All but Pt-alumina (Experiment 7) were first pretreated (regenerated) at 482°C in dry air for 1.5 hours, purged, and further pretreated at 565°C in dry H_2 for one hour. Pt-alumina was pretreated in dry H_2 for one hour at 565°C.

[c] Based on liquid product and reaction effluent GC analyses. The analyses were corrected for feed impurities.

[d] Over a 300-foot Ucon LB-550-X polypropylene glycol capillary column (0.02-inch I.D.), operated isothermally at 75°C, in an Aerograph Model 1520 gas chromatograph.

[e] In addition to dimethylindans, some of these compounds may be 2-ethylindan, phenylcyclopentane or isomeric phenylpentenes (all with MW of 146).

[f] In addition to dimethylindenes, some of these compounds may be ethylindenes other than 1-ethylindene, phenylcyclopentane, or phenylpentadienes (all with MW of 144).

[g] Include dialkylbenzenes, phenylpentenes, and unidentified components.

TABLE 2

Reactions of 2-Phenylpentane over Different Catalysts[a]

Catalyst[b]	Chromia-Alumina Potassia	Platinum (2%) on Silica Gel		Platinum (2%) on Silica-Alumina	Silica-Alumina
Experiment No.	12	13	14	15	16
Reaction Temperature, °C	371	371	371	371	427
Liquid Hourly Space Velocity	6.8	13.2	6.8	6.8	6.8
Residence Time, Seconds	0.43	0.22	0.43	0.43	0.40
Product Composition, Moles Per 100 Moles of Feed[c]					
Unreacted 2-Phenylpentane	98.02	98.67	96.27	44.66	13.73
Benzene	0.60	0.13	0.32	29.20	80.80
Toluene	0.006	0.001	0.03	0.20	0.29
Ethylbenzene	0.12	0.05	0.19	4.06	0.72
Styrene	0.01				
Xylenes				0.02	0.34
n-Propylbenzene		0.001	0.02	0.08	0.07
Cumene	0.03	0.01	0.10	0.16	0.34
n-Butylbenzene	0.03	0.01	0.03	0.10	0.07
Isobutylbenzene				0.04	0.16
sec-Butylbenzene	0.13	0.01	0.04	0.01	
1-Methylindan				0.70	0.18
1-Methylindene				0.10	
1-Phenyl-2-Methylbutane		0.26	0.44	0.05	
1-Phenyl-3-Methylbutane		0.07	0.16	3.66	0.24
2-Phenyl-3-Methylbutane	0.09	Trace	0.09		0.09
3-Phenylpentane				2.16	1.11
2-Phenyl-*cis*-2-Pentene	0.26	0.22	0.27	0.13	
Dimethylindan[d]	0.49	0.26	1.06	10.47	0.86
Dimethylindene[e]		0.07	0.39	1.49	0.17
Other[f]	0.21	0.19	0.39	1.08	0.76
1-Methylnaphthalene		0.05	0.20	0.27	0.03
2-Methylnaphthalene				0.25	0.04
C_{12} and Higher Aromatics				1.11	
Methane		0.03	0.06	0.9	
Ethane, Ethylene	0.02	0.01	0.1	0.2	0.2
Propane, Propylene	0.10	0.1	0.2	2.4	3.8
Butanes, Butenes					
Pentanes	0.38	0.1	0.26	24.5	5.5[g]
Pentenes	0.05	0.01	0.02	1.2	68.7
Other Aliphatic Compounds	0.15				8.0

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[a] Reaction conditions: Atmospheric total pressure, an initial hydrogen to feed ratio of 3.0, and an initial hydrocarbon partial pressure of 0.25 atm. In Experiment 13, the feed flow rate was 6.6 ml/hour, and the H_2 flow rate (measured at 25°C and 1 atm) was 46.8 ml/minute. In the other experiments, feed flow rates were 3.42 ml/hour, and H_2 flow rates were 24.3 ml/minute. The experiments were 30 minutes long. Reaction effluent samples were taken at 19 minutes onstream times. Liquid products were collected from the fifth to the last minute of each experiment. The feed was 99.26% pure (by gas chromatography).

[b] We used 0.5 ml 60–100 mesh size catalyst in each experiment. Catalysts were first pretreated (regenerated) at 482°C in dry air for 1.5 hours, purged and further pretreated at 565°C in dry H_2 for one hour.

[c] Based on liquid product and reaction effluent GC and MS analyses. Product analyses were corrected for feed impurities (mostly alkylbenzenes). Products were analyzed over a 300-feed Ucon LB-500-X polypropylene glycol capillary column (0.02-inch I.D.), operated isothermally at 75°C in an Aerograph Model 1520 gas chromatograph.

on alumina, silica-alumina, and chromia-alumina were described earlier (*1*, *2*). In all experiments one-half milliliter 60–100 mesh size catalyst samples were mixed with one-half milliliter 100–200 mesh size Alundum. The fixed bed reactor was a 6.35 mm OD stainless steel tube. Reaction conditions were atmospheric total pressure, and H_2 diluent with an initial H_2-to-feed mole ratio of 3. Reaction temperatures were 370°C, 427°C, and 482°C. Liquid hourly space velocities were 6.8 or 13.2. The experiments were 20 or 30 minutes long. Reaction effluent samples were taken at 20-minute onstream times (15 minutes in Experiments 1 and 3). Liquid products were collected in an acetone-dry ice condenser from the fifth to the last minute of each experiment.

Conversion data were based on liquid product and reaction effluent gas chromatographic analyses (Tables 1 and 2). We used a 300-foot long Ucon LB-550-X polypropylene glycol capillary column (0.02-inch ID). This column was operated isothermally at 75°C in an Aerograph Model 1520 gas chromatograph. Analyses were corrected for feed impurities. Most components were identified by the GCMS technique, combining a high resolution mass spectrometer (AEI-MS-9) with an F and M Model 810 Research Chromatograph. Some of the unknown products were identified using procedures described earlier (*1*, *3*). We were unable to identify the exact configuration of several phenylpentene, dimethylindan, and dimethylindene isomers. These are combined in Tables 1 and 2. Relative gas chromatographic retention times of the identified hydrocarbons are shown in Table 1.

Liquid products of the *n*-pentylbenzene experiments were analyzed by low voltage mass spectroscopy also (Table 3). Test conditions were: 8.0 volts ionizing potential, 3.0 volts repeller potential, giving an actual ionizing potential of 9.5 volts. The ionizing current was 20 microamps.

Of the 2-phenylpentane experiments, only No. 15 was subjected to low voltage MS analysis. The composition in mole percent is: 30.2 benzene, 1.5 toluene, 4.4 ethylbenzene, 0.2 propylbenzenes, 0.1 indan, 0.1 butylbenzenes, 0.6 methylindans, 0.1 methylindenes, 42.9 pentylbenzenes, 13.6 phenylpentenes plus dimethylindans, 4.2 dimethylindenes, 1.21 methylnaphthalenes, 0.1 hexylbenzenes, 0.3 trimethylindans, 0.2 trimethylindenes, 0.2 dimethylnaphthalenes, 0.1 tetramethylindans, and traces of naphthalene and trimethylnaphthalenes.

RESULTS

n-Pentylbenzene

Dehydrogenation

Dehydrogenation of *n*-pentylbenzene produces 1-phenylpentenes. Gas chromatographic analyses show six of the seven possible isomers. Only one isomer, *trans*-1-phenyl-1-pentene, is identified positively. The other five isomers are listed in order of increasing gas chromatographic retention times (Table 4). If 1-phenylpentene and 1-phenylbutene isomers have similar distributions and *cis/trans* ratios, then Isomer A is *cis*-1-phenyl-1-pentene, Isomers B and C are *trans*-1-phenyl-2 and 3-pentenes, and Isomers D and E are the corresponding *cis* isomers. The seventh possible isomer, 5-phenyl-1-pentene, would be unstable and would not be present at a concentration high enough to be detected.

The phenylpentene isomers probably are in equilibrium in the products of the first seven experiments. Thermodynamic data to calculate equilibrium distributions are unavailable. Experimental distributions at two temperatures are shown in Table 4. At 370°C total conversions and isomer dis-

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[d] In addition to dimethylindans, some of these compounds may be 2-ethylindan, phenylcyclopentane, or isomeric phenylpentenes (all with MW of 146).

[e] In addition to dimethylindenes, some of these compounds may be ethylindenes, phenylcyclopentene, or phenylpentadienes (all with MW of 144).

[f] Includes *n*-pentylbenzene, dialkylbenzenes, phenylbutenes, and unidentified components.

[g] Mostly (about 98%) isopentane.

TABLE 3

Low Voltage MS Analyses[a] of Reaction Products Formed from *n*-Pentylbenzene over Different Catalysts[b]

Catalyst		Chromia-Alumina			2% Pt on Silica Gel				0.75% Pt-Al_2O_3	2% Pt on SiO_2-Al_2O_3			SiO_2-Al_2O_3
Temperature, °C		371	371	427	371	371	427	482	371	371	427	482	427
LHSV		13.2	6.8	6.8	13.2	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8
Experiment No.		1	1A	2	3	4	5	6	7	8	9	10	11
Mole Percent of Liquid Products Component	MW												
Benzene	78	0.1	0.1	0.2	0.2	0.4	0.7	1.2	1.4	0.8	1.2	3.6	4.4
Toluene	92	0.1	0.1	0.1	0.2	0.3	0.6	1.0	0.4	0.1	0.3	0.2	
Ethylbenzene	106	0.2	0.2	0.2	0.2	0.4	0.7	1.3	0.8	0.2	0.3	0.8	0.2
Propylbenzene	120	0.1	0.1	0.1	0.1	0.2	0.5	0.8	0.2	0.1	0.1	0.1	0.1
Methylstyrenes, Indan	118	Trace		0.1	Trace	0.1	0.4	1.0	0.1	0.1	0.2	0.4	
Indene	116						0.1	0.6				0.1	
Butylbenzenes	134	Trace	Trace	Trace	Trace	0.2	0.4	0.9	0.2	Trace	Trace	0.1	Trace
Phenylbutenes, Methylindan	132	Trace		Trace	0.1	0.2	0.5	0.9	0.2	0.1	0.2	0.3	
Methylindenes	130					Trace	0.3	1.5	Trace		0.1	0.4	
Naphthalene	128					0.1	0.3	0.9	Trace	0.2	0.3	0.7	
Pentylbenzenes	148	98.9	98.8	95.5	96.8	90.6	77.0	58.1	88.0	52.8	33.8	34.6	94.3
Phenylpentenes, Ethylindan	146	0.6	0.7	3.6	1.8	4.8	9.7	14.3	5.0	5.3	8.2	9.2	0.8
Ethylindenes	144			0.1	0.2	0.6	4.0	10.8	0.7	0.8	2.0	3.7	0.1
Methylnaphthalenes	142			0.1	0.4	2.1	4.4	6.7	3.0	39.3	52.2	44.2	0.1
Other (MW = 156, 158, 160, 162, 170, 254, and 256)							0.4			0.2	1.1	1.6	

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[a] Test conditions = 8.0 volts ionizing potential, 3.0 volts repeller potential, giving an actual ionizing potential of 9.5 volts. The ionizing current was 20 microamps.

[b] The results above were corrected for the fragmentation of *n*-pentylbenzene (giving mass peaks corresponding to 0.4% benzene and 11.1% toluene) during the M.S. analysis.

TABLE 4

DISTRIBUTION OF THE 1-PHENYLPENTENE ISOMERS IN THE REACTION PRODUCT OF n-PENTYLBENZENE

	Relative[a] GC Retention Times	Catalyst								
		Cr_2O_3-Al_2O_3		Pt-SiO_2			Pt-Al_2O_3	Pt-SiO_2-Al_2O_3[b]	Average	
Temperature, °C		371	427	371	371	427	371	427	371	427
LHSV		13.2	6.8	13.2	6.8	6.8	6.8	6.8		
Experiment		1	2	3	4	5	7	9		
Total 1-Phenylpentenes, Moles Per 100 Moles Feed		0.58	3.77	0.59	0.59	2.85	0.55	0.60		
Isomer Distribution, % of Total 1-Phenylpentenes										
trans-1-Phenyl-1-pentene	35.3	33	36	34	33	38	33	36	34	37
A (*cis*-1-phenyl-1-pentene)	18.4	4	5	8	8	7	4	10	6	6
B (*trans*-1-phenyl-2 or 3-pentene)	19.3	22	19	19	20	16	20	17	20	17
C (*trans*-1-phenyl-2 or 3-pentene)	20.0	17	21	17	17	21	18	17	17	21
D (*cis*-1-phenyl-2 or 3-pentene)	21.15	10	8	10	10	7	11	8	10	8
E (*cis*-1-phenyl-2 or 3 pentene)	21.55	14	11	12	12	11	14	12	13	11

[a] Relative to toluene.

[b] Not included in average.

TABLE 5
DEHYDROGENATION EQUILIBRIUM CONSTANTS FOR THE REACTION
n-PENTYLBENZENE $\leftrightarrows$ *trans*-1-PHENYL-1-PENTENE + H_2

Reaction Temp., °C	Catalyst	LHSV	Experiment No.	Equilibrium Constant
371	Chromia-Alumina	13.2	1	0.00143
	Pt-Silica Gel	13.2	3	0.00156
	Pt-Silica Gel	6.8	4	0.00160
	Pt-Alumina	6.8	7	0.00152
427	Chromia-Alumina	6.8	2	0.01083
	Pt-Silica Gel	6.8	5	0.01085
482	Pt-Silica Gel	6.8	6	0.0475

tributions are about equal over three different catalysts and within a twofold change of space velocity (Experiments 1, 3, 4, and 7, Table 4). Dehydrogenation and olefin isomerization rates over chromia-alumina and platinum on silica gel or alumina carriers are very fast. Dehydrogenation conversions over these catalysts are limited by thermodynamic equilibrium. Equilibrium constants determined from our experimental results are shown in Table 5. Volume changes due to cracking, hydrogen formed and consumed by cyclization, hydrogenolysis, and other reactions were considered in these calculations. Experimental equilibrium constants calculated for the *n*-pentylbenzene $\rightleftharpoons$ *trans*-1-phenyl-1-pentene reaction (Table 5) are very similar to experimental equilibrium constants (*2*) for the *n*-butylbenzene $\rightleftharpoons$ *trans*-1-

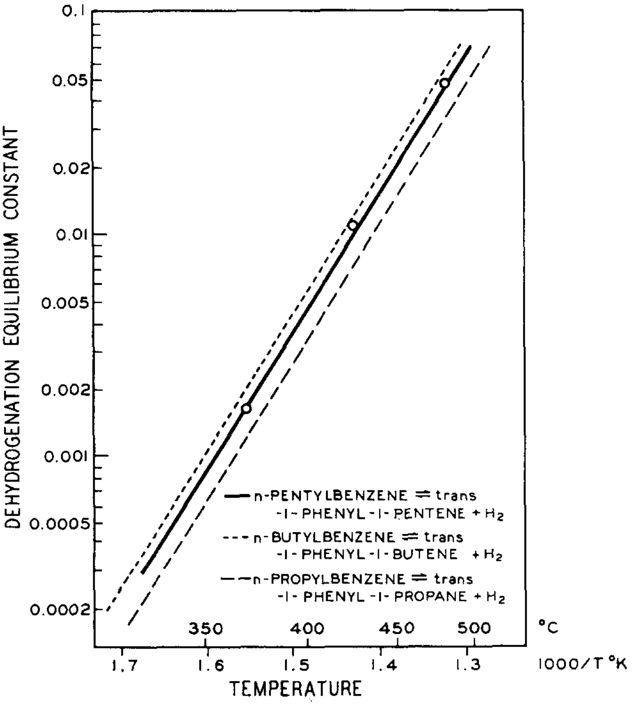
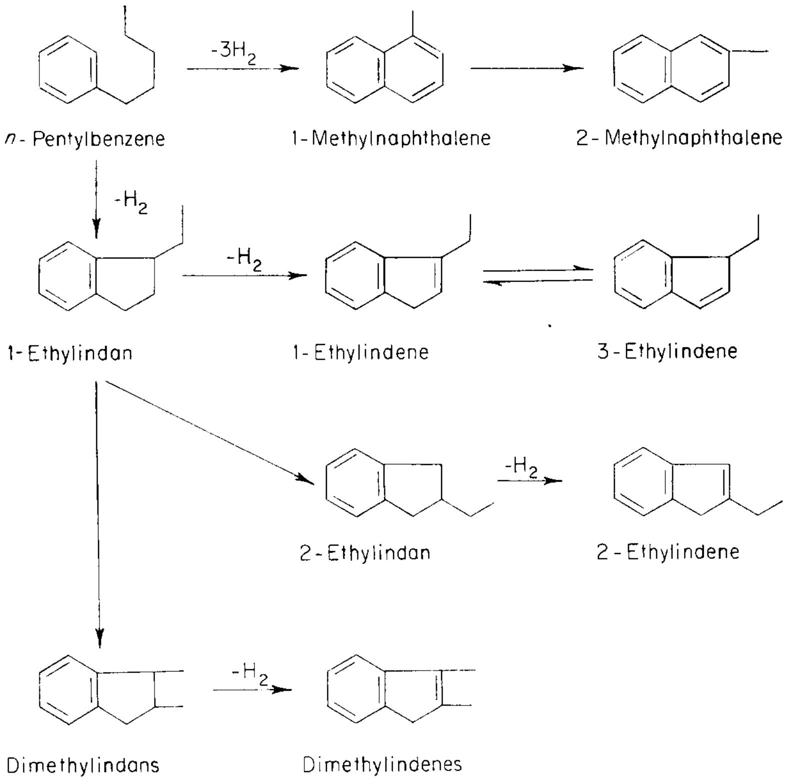


FIG. 1. Dehydrogenation equilibria of alkylbenzenes.

phenyl-1-butene reaction and to calculated equilibrium constants (*2*, *4*) for the n-propylbenzene $\rightleftharpoons$ *trans*-1-phenyl-1-propene reaction. The three log *K*-versus-1/*T* curves are parallel (Fig. 1). Over platinum on silica-alumina dehydrogenation conversions are lower. Concentrations of *trans*-1-phenyl-1-butene at 371°C, 427°C, and 482°C temperatures are only 95%, 47%, and 12% of the equilibrium value. The equilibrium level is approached less and less with increasing temperature. Cyclization of phenylbutenes is very fast over silica-alumina (*5*). The rate of acid-catalyzed reactions might approach dehydrogenation rates, consuming the phenylpentenes almost as fast as they are formed. The results over silica-alumina show an extreme example of this case. Only a trace amount of phenylpentene is present in the reaction product (Experiment 11, Table 1). Phenylpentenes, which are formed very slowly, are consumed almost quantitatively by acid-catalyzed reactions.

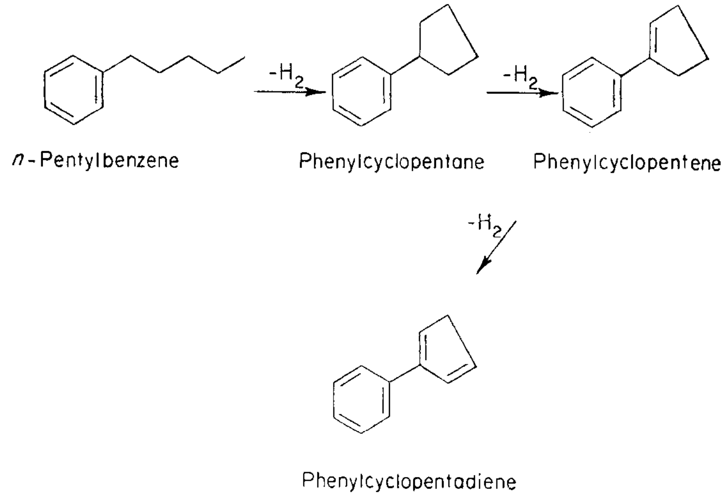
Dehydrocyclizations

The primary products of n-pentylbenzene cyclization are 1-ethylindan, 1-ethylindenes, 1-methyltetralin, and 1-methylnaphthalene. Secondary (consecutive) isomerization may produce dimethylindans, 2-ethylindan, the corresponding indenes, and 2-methylnaphthalene:



Cracking or hydrogenolysis of any of these bicyclic hydrocarbons may yield naphthalene, indan, methylindans, and methylindenes. Transalkylation over the strongly acidic platinum silica-alumina catalyst produces some C_{12} and C_{13} indans, indenes, and naphthalenes. Cyclization to five-membered rings forms the alkylindans and indenes; cyclization to six-membered rings gives tetralins and naphthalenes. With n-pentylbenzene both reaction types involve the addition of a secondary carbon atom to the aromatic ring.

Phenylcyclopentane, phenylcyclopentene, and phenylcyclopentadiene may be formed by a different type of cyclization reaction:



The GCMS technique could not reliably differentiate between phenylcyclopentane, dimethylindans, and 2-ethylindan. The ambiguity is similar with the dimethylindenes, 2-ethylindene, and phenylcyclopentenes. Components with a molecular weight of 146 are called "dimethylindans." Compounds with a molecular weight of 144 are called "dimethylindenes."

Dehydrocyclization rate constants are shown in Table 6. We assumed first-order kinetics in our calculations. Over platinum on silica-gel catalyst cyclization to both five- and six-membered rings occurs. Cyclization to naphthalene has higher activation energy than cyclization to five-membered ring products (*1*). Thus, k_5/k_6 ratios decrease with increasing temperature. With *n*-butylbenzene feed at atmospheric total pressure and with initial H_2 to hydrocarbon molar ratios around 3, the two rates are equal at about 410°C (*1*). The k_5/k_6 ratio is higher for *n*-pentylbenzene than for *n*-butylbenzene even if only the *n*-pentylbenzene → 1-ethylindan + 1-ethylindene reaction is included in the rate constant (k'_5 in Table 7). The rate of *n*-pentylbenzene cyclization to methylnaphthalene is lower than the rate of the *n*-butylbenzene → naphthalene reaction (Table 7). Perhaps the primary carbon of the *n*-butylbenzene side chain has higher reactivity in Pt-catalyzed cyclization than the secondary carbon of *n*-pentylbenzene. This clearly rules out the possibility of an acid-type mechanism over platinum metal.

In *n*-pentylbenzene the side-chain carbons involved in cyclizations leading to five- and six-membered products have similar structures (i.e., both are secondary). The high k'_5/k_6 ratios observed suggest that, other things being equal, platinum-catalyzed cyclization favors the five-membered product. However, the difference between the two processes is small and may be inverted by changing process conditions (e.g., by increasing reaction temperature). Alkyl side chains may be wholly or partially removed from the bicyclic products of cyclization. Naphthalene, indan, indene, methylindan, and methylindenes are the products of this hydrogenolysis (Table 6). The relative proportion of bicyclics dealkylated increases with increasing temperature. At 371°C, 426°C, and 482°C temperatures 5%, 6%, and 12% of the cyclization product is dealkylated.

The different alkylindans are at equilibrium with the corresponding alkylindenes. At constant temperature alkylindan/alkylindene ratios over platinum on silica gel are very similar (Table 6). For example, methylindan/methylindene ratios are exactly the same in our *n*-pentylbenzene and *n*-butylbenzene experiments (2.8 at 427°C and 0.96 at 482°C).

Isomerization of 1-methylnaphthalene

TABLE 6

DEHYDROCYCLIZATION OF n-PENTYLBENZENE AT AN LHSV OF 6.8

Catalyst	Pt on Silica Gel			Pt on Alumina	Pt on Silica-Alumina			Silica-Alumina
Temperature, °C	371	427	482	371	371	427	482	427
Cyclization Products, Moles Per 100 Moles of Feed								
Indan + Indene	0.11	0.25	0.40	0.04	0.03	0.14	0.21	
1-Methylindan + Methylindenes	0.19	0.53	0.92	0.15	0.04	0.26	0.41	0.02
1-Ethylindan + Ethylindene	4.10	6.85	4.99	3.40	1.37	1.50	0.98	0.33
Dimethylindans + Dimethylindenes	1.25	3.32	5.36	1.00	3.17	6.95	8.49	0.81
C_{12} and C_{13} Indans + Indenes						0.10	0.20	
Naphthalene	0.06	0.23	0.90	0.03	0.10	0.32	0.58	
Methylnaphthalenes	1.95	4.53	6.30	2.82	37.82	50.96	41.99	0.14
Dimethylnaphthalenes and Higher					0.20	0.70	1.30	
First Order Cyclization Rate Constants, Sec^{-1}								
k_5 (to Indans and Indenes)	0.138	0.305	0.367	0.113	0.142	0.36	0.42	0.030
k_6 (to Naphthalenes)	0.049	0.133	0.227	0.071	1.170	2.08	1.80	0.0036
k_5/k_6	2.80	2.30	1.62	1.61	0.12	0.17	0.23	8.30
1-Methylindan/Methylindene		2.8	0.96	7		2.3	1.2	∞
Dimethylindans/Dimethylindenes	7	2.9	0.7	8	34	11.6	7	80
1-Ethylindan/1-Ethylindene	12	3.5	0.96	18	26	5	2.6	∞
1-Methylnaphthalene/2-Methylnaphthalene	48	44	30	22	2.7	1.37	0.71	0.6
1-Ethylindan/Dimethylindans	3.5	2.2	1.1	3.6	0.4	0.2	0.1	0.4
1-Ethylindene/Dimethylindenes	2.0	1.8	0.8	1.6	0.6	0.5	0.3	

TABLE 7

Comparison of the Cyclization of Alkylbenzenes over Platinum on Silica Gel

Hydrocarbon Feed	n-Pentylbenzene		n-Butylbenzene		2-Phenylpentane
Temperature, °C	371	427	371	427	371
First Order Cyclization Rate Constants					
k_5 (All Five-Membered Ring Products Included)	0.14	0.31	0.12	0.48	0.034
k'_5 (Only 1-Ethylindan and 1-Ethylindene Included)	0.10	0.19			
k_6	0.05	0.13	0.08	0.52	0.0047
k_5/k_6	2.8	2.3	1.46	0.92	7.3
k'_5/k_6	2.0	1.4			

to 2-methylnaphthalene is very slow over platinum on silica gel. The amount of 2-methylnaphthalene is between 2% and 3% of the total methylnaphthalenes formed.

Over platinum on silica-alumina n-pentylbenzene and n-butylbenzene have similar rates of cyclization to five-membered rings (Table 8). However, over this and similar acidic dehydrogenation catalysts the longer side chain of n-pentylbenzene has an interesting consequence in determining cyclization rates to naphthalenes. The dehydrocyclization product obtained from n-butylbenzene over platinum on silica-alumina is mostly methylindan. Naphthalene cannot be formed from n-butylbenzene by acid-catalyzed cyclization because its formation would involve a primary carbonium ion. The n-pentylbenzene → methylnaphthalene reaction is not inhibited by such unstable intermediates. The reaction proceeds through $C_6H_5\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}C^+H\text{-}CH_3$, a secondary carbonium ion. As a consequence, over platinum on silica-alumina, rates of cyclization to six-membered rings of n-pentylbenzene are 50 to 100 times higher than those of n-butylbenzene (Table 8). Similarly, alkylindan/methylnaphthalene ratios in the reaction product of n-pentylbenzene are 60 to 190 times lower than in the product of n-butylbenzene reactions. These confirm our earlier observation that over acidic dehydrocyclization catalysts the stability of the intermediate carbonium ion determines whether cyclization forms five- or six-membered rings. Over platinum on silica-alumina acid-catalyzed cyclization proceeds through these steps:

> Dehydrogenation of the alkylbenzene over the platinum component, yielding phenylalkenes. Protonation of the phenylalkene over the acid component forming a carbonium ion. Attack of this carbonium ion on the aromatic ring, closing either a five- or six-membered ring. Stabilization of the

TABLE 8

Comparison of the Cyclization of Alkylbenzenes over Platinum on Silica-Alumina

Hydrocarbon Feed	n-Pentylbenzene		n-Butylbenzene		2-Phenylpentane
Temperature, °C	371	427	371	427	371
First Order Cyclization Rate Constants					
k_5	0.14	0.36	0.18	0.39	0.45
k_6	1.17	2.08	0.008	0.04	0.025
k_5/k_6	0.12	0.17	22.6	10.5	18

product by proton elimination or hydride abstraction. This step may be followed by dehydrogenation to the thermodynamically most stable species (e.g., to an alkylnaphthalene in the case of six-membered ring closure).

Over platinum on silica-alumina k_5/k_6 ratios with *n*-pentylbenzene are very low (Table 8). This suggests that if the possible carbonium ion intermediates leading to five- or six-membered ring closure have similar structures (e.g., both are secondary carbonium ions, as in the case of *n*-pentylbenzene), acid-catalyzed cyclization favors six-membered ring products. The selectivity is kinetically controlled. Isomerization between methylindan and tetralin is extremely slow (*6*). Isomerization between ethylindan and methylnaphthalene is probably not much faster. The k_5/k_6 ratio of 2-phenylpentane over platinum silica-alumina, as we will show later, is about the same as the k_5/k_6 ratio of *n*-butylbenzene. Should a fast methylnaphthalene $\rightleftharpoons$ alkylindan isomerization exist, the k_5/k_6 ratios of 2-phenylpentane and *n*-pentylbenzene would be similar.

Dealkylation of the bicyclic products is *slower* over platinum on silica-alumina than over platinum on silica gel. This suggests hydrogenolysis as the main process dealkylating short (= one or two carbon length) side chains of aromatics. Over the platinum on silica-alumina alkylindan dealkylation amounts to 1.5%, to 6.0% of the total alkylindans present. Methylnaphthalene dealkylation is between 0.3% and 1.3%.

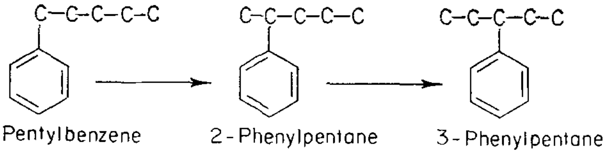
Isomerization of 1-methylnaphthalene to 2-methylnaphthalene is very intensive (Table 6). At 482°C the 1-methylnaphthalene/2-methylnaphthalene ratio is less than one. This isomerization is clearly an acid-catalyzed reaction. (The ratio was above 30 over platinum on silica gel.) Similarly, 1-ethylindan/dimethylindans and 1-ethylindene/dimethylindenes ratios are much lower over the silica-alumina supported catalyst than over platinum on silica gel (Table 6).

Platinum on alumina has properties between those of platinum on silica gel and platinum on silica-alumina. The rate of cyclization to five-membered ring is somewhat lower over the 0.75% platinum on alumina than over the 2% platinum on silica gel (Table 6). The k_5/k_6 ratio (1.6 at 371°C) falls between those observed over the silica gel (2.8) and silica-alumina (0.12) supported catalysts. The isomerization of 1-methylnaphthalene is substantially slower over the alumina-supported catalyst than over platinum on silica-alumina. At 371°C the 1-methylnaphthalene/2-methylnaphthalene ratio is 22 over platinum on alumina and 2.7 over platinum on silica-alumina.

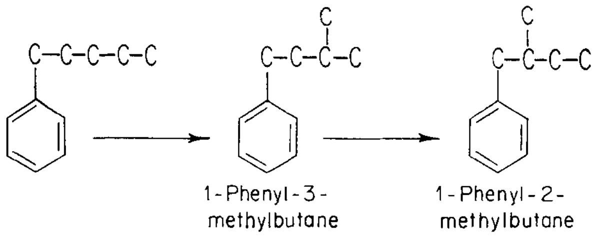
Cyclization is slow over silica-alumina. Most of the products are unidentified "dimethylindans." Isomerization of 1-methylnaphthalene is very extensive.

Isomerization

Skeletal isomerization of the alkyl side chain of *n*-pentylbenzene produces 2- and 3-phenylpentanes, 1-phenyl-2- and 1-phenyl-3-methylbutanes, and 2-phenyl-3-methylbutane. All isomers may be produced over the acidic catalysts (silica-alumina, platinum on alumina, and platinum on silica-alumina, Table 1). The reactions probably involve carbonium ion intermediates. 2- and 3-Phenylpentanes may be produced by successive phenyl migration steps:



Methyl migration might produce 1-phenyl-2- and 1-phenyl-3-methylbutanes. The latter compound is usually present at a higher concentration. This suggests a stepwise reaction mechanism involving successive 1-2 methyl shifts:

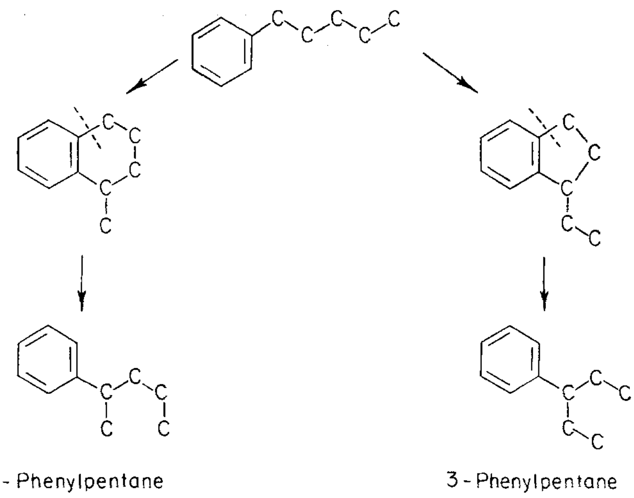


Both phenyl and methyl shifts may be involved in the formation of 2-phenyl-3-methylbutane. The acid-catalyzed cracking of secondary alkylbenzenes (2- and 3-phenylpentanes and 2-phenyl-3-butane) is very fast. Relative conversion levels of these isomers therefore may not represent true isomerization rates over acidic catalysts.

TABLE 9
Isomerization of *n*-Pentylbenzene over Platinum on Silica Gel Catalyst

Temperature, °C	371		427	482
LHSV	13.2	6.8	6.8	6.8
Isomerized Monoalkylbenzenes				
Moles/100 Moles of Feed	0.27	0.54	1.02	1.14
Moles/100 Moles of Total Monoalkylbenzenes	0.28	0.60	1.31	1.75
Distribution, % of Total Isomerized Monoalkylbenzenes				
2-Phenylpentane	33	33	61	53
3-Phenylpentane	30	30	21	23
1-Phenyl-2-methylbutane	7	11	7	9
1-Phenyl-3-methylbutane	30	19	11	11
2-Phenyl-3-methylbutane	Trace	7	Trace	4

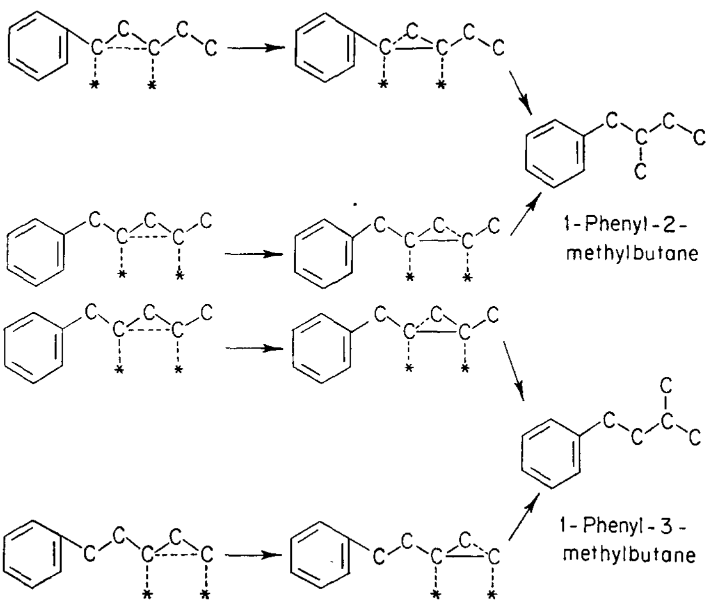
Isomerization over the neutral platinum on silica gel catalyst proceeds by different processes (Table 9). Two mechanisms were recognized in our *n*-butylbenzene study (*1*). One involves cyclic intermediates, the other proceeds by a noncarbonium ion-type 1-2 methyl shift. The same processes may operate with *n*-pentylbenzene. Cyclic intermediates may be involved in the formation of 2- and 3-phenylpentanes:



Isomerization through cyclic intermediates increases with increasing temperature relative to other types of isomerization (Table 9).

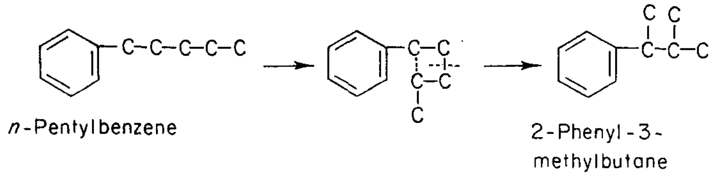
Small amounts of dialkylbenzenes may be produced also by such sequential cyclization and ring-opening steps. The mechanism is similar to the one proposed by Shephard and Rooney for the 1-methyl-2-ethylbenzene $\rightleftarrows$ *n*-propylbenzene reactions (*7*). In our product analyses, dialkylbenzenes are combined under "Other Aromatic Compounds" (Table 1).

1-Phenyl-2- and 1-phenyl-3-methylbutanes might be formed by 1-2 methyl shifts (surface sites are represented by *):



Such 1-2 methyl shifts over platinum on neutral supports were previausly described by Barron, Maire, Muller, and Gault (*8*), and Anderson and Avery (*9*).

2-Phenyl-3-methylbutane may be the product of two successive isomerization steps. An isomerization process involving 1-4 diadsorbed intermediates cannot be excluded:



The platinum and acid-catalyzed isomerization processes may both contribute to overall isomerization over the platinum-alumina and the platinum silica-alumina catalysts. Isomerization rates of *n*-pentylbenzene are similar to those of *n*-butylbenzene over the platinum-containing catalysts.

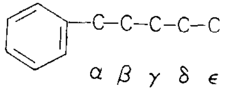
Fragmentation

Acid-catalyzed cracking and platinum-catalyzed hydrogenolysis are the two types of fragmentation processes observed in this study. In cracking, one of the products is an olefin. A molecule of hydrogen is added in hydrogenolysis, and no olefin is formed. In the presence of hydrogen over a hydrogenating catalyst, the olefinic products of cracking could be completely saturated.

Cracking is the only type of fragmentation over silica-alumina. The reaction is very similar to that observed with *n*-butylbenzene (*1*). More than 70% of the total *n*-pentylbenzene reaction is

TABLE 10

Fragmentation of n-Pentylbenzene. Distribution of Products, as Percents of Total Fragmentation



Catalyst		Platinum on Silica Gel				$Pt-Al_2O_3$	Pt on Silica-Alumina			Silica-Alumina
Temperature °C		371		427	482	371	371	427	482	427
LHSV		13.2	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8
Experiment No.		3	4	5	6	7	8	9	10	11
Position	*Products of Fragmentation*									
Phenyl – α	Benzene + Pentane, Pentenes	27	26	19	22	40	73	58	69	96
α – β	Toluene + Butane, Butenes	22	18	17	18	18	9	14	9	1.4
β – γ	Ethylbenzene, Styrene + Propane, Propylene	21	21	31	31	25	12	19	17	2.3
γ – δ	n-Propylbenzene + Ethane, Ethylene	14	16	17	14	8	2	5	3	0.2
δ – ε	n-Butylbenzene + Methane	16	19	16	15	9	4	4	2	0.1
Total Fragmentation Products, Moles Per 100 Moles of n-Pentylbenzene Feed		0.73	1.39	2.26	5.09	2.28	0.87	1.85	4.94	4.18

cracking. Most of the scission (i.e., 96%) occurs between the phenyl ring and the alpha carbon atom (Table 10). Benzene and pentenes are produced; part of the pentene is hydrogenated. The (pentenes + pentanes)/benzene ratio is 0.95 (Table 1). This shows that most of the pentenes do not readsorb and crack further.

Hydrogenolysis over platinum on silica gel is not selective. Similar quantities of benzene, toluene, ethylbenzene, *n*-propylbenzene, and *n*-butylbenzene (plus the corresponding C_1-C_5 paraffins) are formed (Tables 1 and 10). The total rate of hydrogenolysis is between one-third and one-seventh of the rate of total cyclization. The distribution of the products of hydrogenolysis is similar to that observed with *n*-butylbenzene. At higher temperatures (427–482°C) scission between the second and third carbon atoms of the side chain becomes more important (Table 10). Ethylbenzene and propane are produced in this process. Changing space velocity has very little effect on the distribution of hydrogenolysis products (Experiments 3 and 4, Table 10).

Acid-catalyzed cracking and platinum-catalyzed hydrogenolysis proceed simultaneously over platinum on alumina and platinum on silica-alumina. The distribution of the scission products is determined by the relative strength of the acidic and metal-type catalytic components.

Separate contributions of the acid-catalyzed cracking and platinum-catalyzed hydrogenolysis may be calculated in a manner similar to that used in our *n*-butylbenzene study (*1*). Over platinum-alumina, hydrogenolysis is responsible for three-fourths of the overall fragmentation. Between one-third and one-half of the total fragmentation proceeds by hydrogenolysis over platinum on silica-alumina.

Transalkylation

Higher molecular weight bicyclic aromatics are formed by acid-catalyzed methyl or ethyl transfer reactions (disproportionation) over platinum on silica-alumina. Low voltage MS analyses show C_{12} and C_{13} alkylnaphthalenes and other hydrocarbons in Experiments 8, 9, and 10 (Table 3). Trans-alkylation mostly affects the naphthalene derivatives.

2-Phenylpentane

Dehydrogenation

The only positively identified dehydrogenation product of 2-phenylpentane is 2-phenyl-*cis*-2-pentene. Equilibrium dehydrogenation conversions may be assumed over the chromia-alumina and platinum-silica gel catalysts (Experiments 12, 13, and 14, Table 2). The experimental equilibrium constant for the 2-phenylpentane $\rightleftharpoons$ 2-phenyl-*cis*-2-pentene + H_2 reaction at 371°C is 0.002. The corresponding reaction with *n*-butylbenzene (forming *trans*-1-phenyl-1-butene) has the same equilibrium constant (*1*).

Dehydrocyclization

The primary products of the cyclization of 2-phenylpentane are *cis*- and *trans*-1,3-dimethylindans, 1,3-dimethylindene, 1-methyltetralin, and 1-methylnaphthalene.

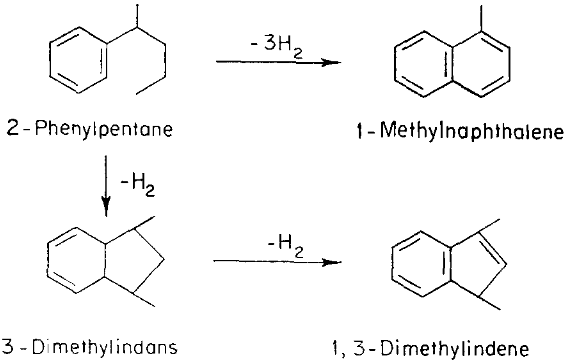
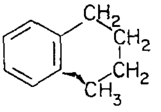


TABLE 11
Dehydrocyclization of 2-Phenylpentane at an LHSV of 6.8

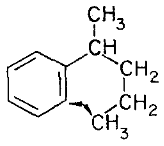
Catalyst Temperature, °C	Pt on Silica Gel 371	Pt on Silica-Alumina 371	Silica-Alumina 427
Cyclization Products, Moles Per 100 Moles of Feed			
1-Methylindan + 1-Methylindene		0.80	0.18
Dimethylindans, Ethylindans + Indenes	1.45	11.96	1.03
C_{12}-C_{13} Alkylindans + Indenes		0.06	
Naphthalene		Traces	
Methylnaphthalenes	0.20	0.52	0.07
Di- and Trimethylnaphthalenes		0.21	
Total Alkylindans and Indenes	1.45	13.36	1.21
Total Alkylnaphthalenes	0.20	0.73	0.07
First Order Cyclization Rate Constants, Sec^{-1}			
k_5 (to Indans and Indenes)	0.034	0.45	0.07
k_6 (to Naphthalenes)	0.0047	0.025	0.0004
k_5/k_6	7.3	18	17
1-Methylnaphthalene/2-Methylnaphthalene	∞	1.08	0.8

Other dimethylindans, ethylindans, the corresponding indenes, and 2-methylnaphthalene may be formed by consecutive isomerization of the primary cyclization products. Cyclization to five-membered rings involves the addition of a secondary carbon atom to the aromatic ring. Dimethylindans and dimethylindenes are not identified separately. Dehydrocyclization rate constants are calculated assuming first order kinetics (Table 11).

Both cyclization to five- and six-membered rings occurs over platinum on silica gel. Cyclization rates are lower for 2-phenylpentane than for *n*-pentylbenzene or *n*-butylbenzene (Table 7). Side-chain carbon atoms involved in the cyclizations of *n*-butylbenzene and 2-phenylpentane have identical nature (i.e., secondary in five-membered ring closure and primary in six-membered ring closure). The difference between the two molecules—the extra methyl group—is far removed from the two carbon atoms reacting:



and



The methyl group in a γ position of the side-chain interferes with cyclization over platinum. Deuterium exchange of the two methyl groups of the isopropyl side chain in cumene over nickel films occurs in two steps (*10*). Both methyl groups cannot exchange at the same time. The cumene molecule probably has to leave the surface and readsorb before the second methyl group can exchange. A similar situation might exist over platinum. The phenyl ring is probably held parallel to the surface by π-bond to the metal (*10*). This necessarily limits the number of possible configurations in which the side chain can adsorb. The side chain of 2-phenylpentane may adsorb in one of two ways. Either the methyl group or the propyl group will point away from the surface. Cyclization is possible only in the first case. If adsorption could happen both ways, the rate of cyclization of 2-phenylpentane would be half of that of *n*-butylbenzene. A slight preference for adsorption of the methyl group may explain the observed three-and-a-half fold difference in k_5, the rate constant for cyclization to five-membered ring products (Table 7).

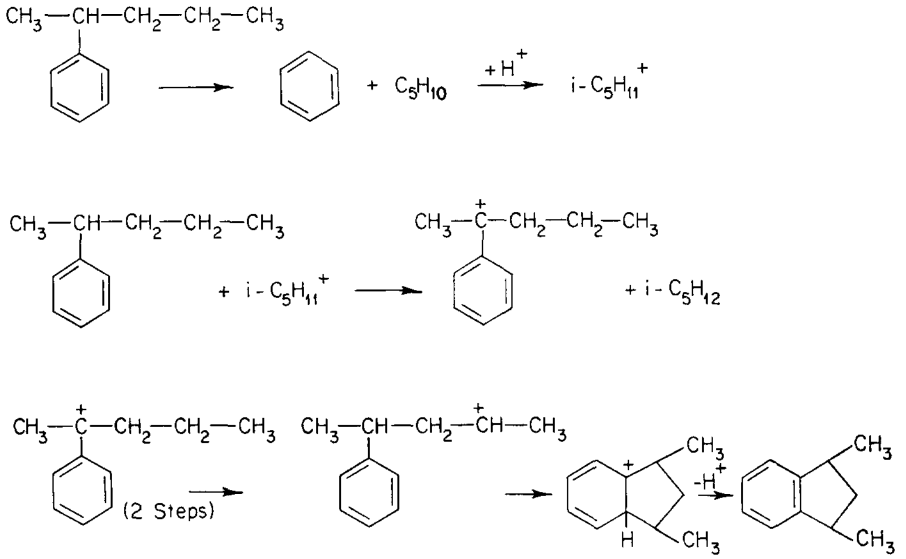
2-Methylnaphthalene is not formed from

2-phenylpentane over platinum on silica gel (Table 2).

The rate of cyclization of 2-phenylpentane over platinum on silica-alumina is two-and-a-half times *faster* than that of *n*-butylbenzene (Table 8). Cyclization on this catalyst occurs mostly by an acid-catalyzed mechanism. Branching of the side chain in 2-phenylpentane could have stabilized the carbonium ion intermediate relative to that of *n*-butylbenzene and thus increase reaction rates. Cyclization to six-membered products (1-methylnaphthalene and naphthalene) would involve primary carbonium ions in the case of 2-phenylpentane. Thus, cyclization to six-membered rings is significantly retarded relative to cyclization to five-membered rings. The k_5/k_6 ratios of 2-phenylpentane and *n*-butylbenzene are very similar (18 and 22.6 at 371°C). The k_5/k_6 ratio of *n*-pentylbenzene differs from these values by a factor of at least 150 (Table 8).

About half of the 1-methylnaphthalene formed from 2-phenylpentane isomerizes to 2-methylnaphthalene over platinum silica-alumina. Dimethylindan (and dimethylindene) isomerization is also considerable (Table 2).

Dehydrocyclization of 2-phenylpentane over silica-alumina is significantly slower than over platinum silica-alumina (1.28% at 427°C versus 14.1% at 371°C). Five-membered ring products predominate; the k_5/k_6 ratio is 17. This cyclization is acid catalyzed. Carbonium ions are formed via protonation of the unsaturated bonds of phenylpentenes. Over silica-alumina, the rate controlling step is olefin formation. Phenylpentenes may be formed by thermal dehydrogenation. Cracking of 2-phenylpentane is very extensive over silica-alumina. Benzene, pentenes, and isopentane are formed (Table 2). Pentyl cations may be produced by protonation of pentenes. Hydride transfer between 2-phenylpentane and a pentyl cation might be another way to generate phenylpentyl cations:

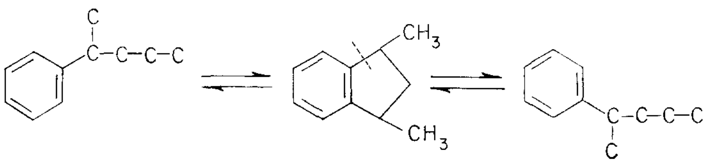


More than half of the 1-methylnaphthalene formed over silica-alumina is isomerized to 2-methylnaphthalene (Table 9).

Isomerization

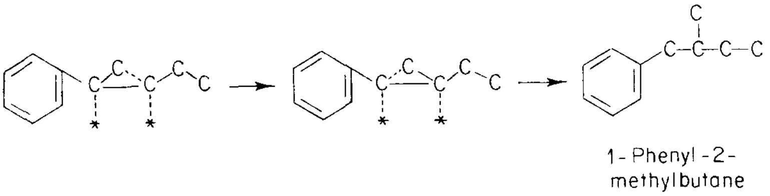
Phenylmethylbutanes, 3-phenylpentane, and traces of *n*-pentylbenzene are formed by side-chain isomerization of 2-phenylpentane. Phenyl migration can produce 3-phenylpentane over the acidic catalysts (Pt silica-alumina and silica-alumina, Table 2). Similarly, successive phenyl and methyl transfers may form the different phenylmethylbutenes over these acidic catalysts.

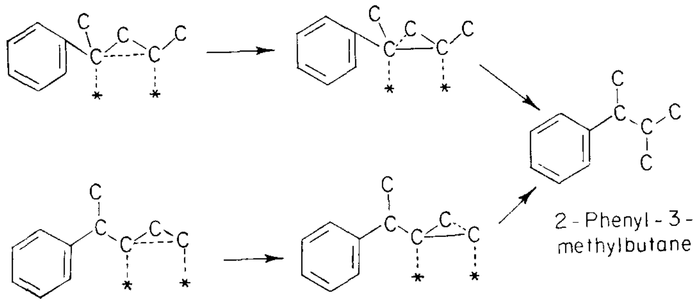
Isomerization over the neutral platinum-silica gel catalyst proceeds by different mechanisms. Isomerization via five-membered cyclic intermediate forms another 2-phenylpentane molecule:



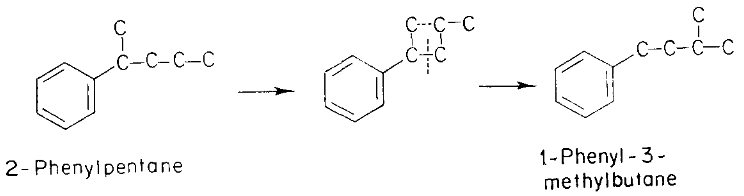
n-Pentylbenzene may be formed through a methyltetralin-type intermediate. We observed only traces of *n*-pentylbenzene.

Over platinum on silica gel 1,3-diadsorbed intermediates might be involved in isomerizations leading to 1-phenyl-2-methylbutane and 2-phenyl-3-methylbutane:





At 371°C, 0.44% of 1-phenyl-2-methylbutane, 0.09% of 2-phenyl-3-methylbutane, and 0.16% of 1-phenyl-3-methylbutane are formed from 2-phenylpentane over platinum-silcia gel. 1-Phenyl-3-methylbutane might be formed through successive isomerization steps. However, an isomerization process involving a 1,4-diadsorbed intermediate is more likely:



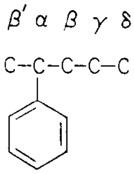
No possible simple, nonacidic mechanism may be written for the 2-phenylpentane ⇄ 3-phenylpentane reaction. We did not observe any 3-phenylpentane in the reaction product of 2-phenylpentane over platinum-silica gel (Table 2). Note that this reaction is the predominant way of isomerization over the acidic catalysts.

2-Phenyl-3-methylbutane is the only isomer formed over chromia-alumina (Table 2). The reaction may involve adsorbed cyclopropane-type intermediates, as proposed by Pines and Goetschell (*11*).

Fragmentation

More than 95% of the total 2-phenylpentane reaction over silica-alumina is cracking. Most of the scission (i.e., 98.6%) occurs between the phenyl ring and the alpha carbon atom (Table 12). This rate

TABLE 12
FRAGMENTATION OF 2-PHENYLPENTANE. DISTRIBUTION OF PRODUCTS, AS PERCENT OF TOTAL FRAGMENTATION



Catalyst		Pt on Silica Gel	Pt on Silica-Alumina	Silica-Alumina	Chromia-Alumina
Temperature, °C		371	371	427	371
Experiment No.		14	15	16	12
Position	*Products of Fragmentation*				
Phenyl – α	Benzene + Pentanes, Pentenes	47	87	98.6	66
α – β	Ethylbenzene + Propane, Propylene	28	12	0.9	14
β – γ	Cumene + Ethane, Ethylene	15	0.5	0.4	3
γ – δ	*sec*-Butylbenzene + Methane	6	0.03	—	14
α – β'	*n*-Butylbenzene + Methane	4	0.3	0.1	3
Total Fragmentation Products, Moles Per 100 Moles of 2-Phenylpentane Feed[a]		0.68	33.52	81.93	0.92

[a] Does not include products formed by more than one fragmentation step (such as toluene, *n*-propylbenzene), and fragmentation products of cyclic compounds (such as methylindan).

of cracking is substantially higher than those observed with *n*-pentylbenzene or *n*-butylbenzene. The bond cleaved in 2-phenylpentane connects the phenyl ring with a tertiary carbon atom. Secondary atoms are involved with the *n*-alkylbenzenes. Part of the pentenes are hydrogenated; the product is isopentane. Another part of the pentenes formed larger MW alkenes and paraffins by polymerization. Only a very small fraction of the pentenes cracks further to smaller aliphatics (Table 2).

Fragmentation over platinum on silica-gel occurs by hydrogenolysis. Hydrogenolysis of 2-phenylpentane also favors breaking the bond between the phenyl ring and the α-carbon atoms of the side shain. Almost half of the total hydrogenolysis involves the scission of this bond. The next most favored position for bond-breaking is between the tertiary carbon atom of the side chain and a secondary carbon. Hydrogenolysis of methyl groups (on either side of the chain) is slow (Table 12).

Hydrogenolysis and cracking proceed simultaneously over platinum on silica-alumina. Of the total fragmentation, 87% occurs between the phenyl ring and the tertiary ("α") carbon of the side chain.

Bonds between carbon atoms with a higher number of substituents have generally higher fragmentation rates over nonacidic chromia-alumina (Table 12). A similar relationship was found by Csicsery and Pines for the hydrogenolysis of C_5-C_8 paraffins (*12*).

Transalkylation

Low voltage MS analysis shows about 1% C_{12} and higher alkylbenzenes, alkylindanes, alkylindenes, and alkylnaphthalenes in the reaction product obtained over platinum on silica-alumina (Table 2). A small amount of fluorene is also observed. Transalkylation probably proceeds by an acidic mechanism.

CONCLUSIONS

Dual functioning catalysts, containing both acidic and dehydrogenation components are used in the reforming process.

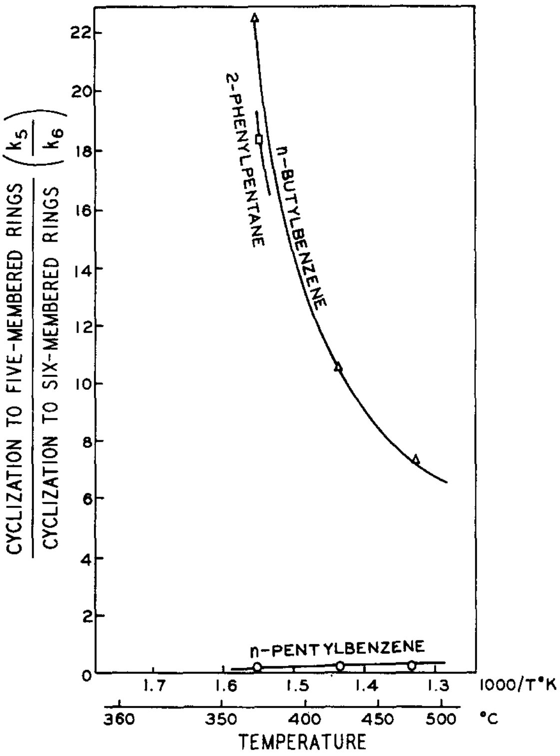


FIG. 2. Cyclization selectivities of alkylbenzenes over platinum (2%) on silica-alumina catalyst.

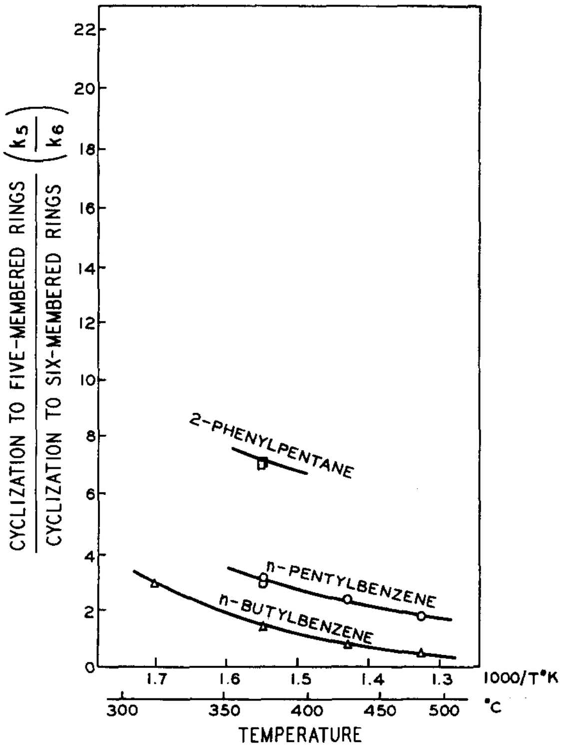


FIG. 3. Cyclization selectivities of alkylbenzenes over platinum (2%) on silica-gel catalyst.

Our experiments with *n*-butylbenzene (*1*) revealed much about reaction mechanisms occurring over these catalysts. A recent set of experiments using *n*-pentylbenzene and 2-phenylpentane furnished further information on this subject. All the new observations indicate that the mechanisms suggested using *n*-butylbenzene as a model compound are correct in every detail. Thus, there are at least two different dehydrocyclization processes over platinum catalysts supported by acidic carriers. The acidic mechanism is a self-alkylation process involving carbonium ion intermediates. The stability of the intermediate carbonium ion determines whether cyclization forms five- or six-membered rings. Acid-catalyzed cyclization produces almost exclusively five-membered rings from 2-phenylpentane and *n*-butylbenzene. Six-membered rings (methylnaphthalenes) are the preferred products in the acid-catalyzed reaction of *n*-pentylbenzene.

Side-chain branchings in 2-phenylpentane increases acid-catalyzed cyclization rates, probably by stabilizing the carbonium ion intermediate. Effects of side-chain structure and length on cyclization selectivity over platinum silica-alumina and platinum silica gel are shown in Figs. 2 and 3.

Cyclization over platium metal proceeds by a different mechanism. Over platinum on silica gel the ratio of five-member ring cyclization to six-member ring cyclization (k_5/k_6) is higher for *n*-pentylbenzene than for *n*-butylbenzene (2.8 versus 1.46 at 371°C). Over platinum on an acidic support (silica-alumina) the opposite holds (0.12 for *n*-pentylbenzene and 22.6 for *n*-butylbenzene). Thus, acid-catalyzed cyclization mechanism over platinum metal is extremely unlikely. Furthermore, rate constants for cyclization to six-membered rings over platinum-silica gel are higher for *n*-butylbenzene (where cyclization occurs between the phenyl ring and a primary carbon atom) than for *n*-pentylbenzene (where the carbon atom involved is *secondary*). This relationship rules out the possibility of any carbonium ion-type cyclization mechanism over platinum metal.

All side-chains isomers are formed over acidic catalysts. Over platinum on silica gel cyclic intermediates lead to 2-, and 3-phenylpentanes from *n*-pentylbenzene. *n*-Pentylbenzene forms 1-phenyl-2-, and 3-methylbutanes, 2-phenylpentane forms 1-phenyl-2-methylbutane, and 2-phenyl-3-methylbutane via 1,3-diadsorbed intermediates over platinum metal. 1,4-Diadsorbed intermediates might be involved over platinum on silica gel in the isomerization of *n*-pentylbenzene to 2-phenyl-3-methylbutane, and in the isomerization of 2-phenylpentane to 1-phenyl-3-methylbutane.

The 1-methylnaphthalene ⇄ 2-methylnaphthalene reaction is very fast over acidic catalysts.

Acid-catalyzed cracking cleaves the bond between the phenyl ring and the α-carbon of the side chains. Cracking rates of secondary alkylbenzenes are about an order of magnitude higher than those of primary *n*-alkylbenzenes.

Platinum-catalyzed hydrogenolysis affects the side-chain bonds of *n*-alkylbenzenes at an approximately equal rate. In secondary alkylbenzenes the bond next to the phenyl ring is cleaved preferentially. Demethylation of branched side chains is slow relative to the scission of the other side-chain bonds.

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