

Catalytic Reactions of Phenylbutenes

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4-Phenyl-1-butene was reacted over pure and alkali-impregnated aluminas, silica-alumina, platinum-silica gel, and chromia-alumina catalysts in the presence of hydrogen. The reactions observed were double-bond and skeletal isomerization, cyclization, hydrogenation, cracking, and hydrogenolysis. Double-bond isomerization may be catalyzed by acids, bases, or metals. Over acidic or basic catalysts, double-bond isomerization occurs stepwise. Skeletal isomerization is mostly acid-catalyzed. Over the platinum catalyst, hydrogenation of double bonds is very much faster than the other reactions. Phenylbutenes and *n*-butylbenzene, therefore, react very similarly over platinum on silica gel. Conversely, over silica-alumina, the rate of cyclization of 4-phenyl-1-butene is about 2000 times higher than that of *n*-butylbenzene. Cyclization here produces methylindan and methylindenes almost exclusively. This confirms the mechanism proposed earlier for the acid-catalyzed cyclization of alkylbenzenes. The carbonium ion intermediates are produced by protonation of the olefinic bonds. Dehydrogenation is the rate-controlling step of alkylbenzene dehydrocyclization over silica-alumina.

Over dual-functioning petroleum reforming catalysts, dehydrogenation of the alkylbenzene to phenylalkenes is the first step in cyclization, isomerization, and fragmentation (1). In this paper, we attempt to clarify the role of the phenylalkene intermediate. We also plan to further confirm the existence of separate acid- and metal-catalyzed mechanisms for these reactions. *n*-Butylbenzene was the feed used in our first study. A dehydrogenation product of *n*-butylbenzene, 4-phenyl-1-butene, was used in the present work.

EXPERIMENTAL

The feed was 4-phenyl-1-butene, purchased from Matheson, Coleman, and Bell Company. Its purity by gas chromatography was 98%. Conversion results were corrected for feed impurities.

To permit comparisons between the *n*-butylbenzene experiments (1) and the present experiments using phenylbutene, experimental conditions were very similar to those used earlier (1). Reaction temperatures were 315°, 371°, and 427°C. The feed flow rate was 3.42 ml/hr; the H₂ flow

rate was 34.2 ml/min. The LHSV was 6.8, and the initial hydrogen-to-hydrocarbon molar ratio was 4:1. This deviated from the 3:1 ratio used in the *n*-butylbenzene test; however, the overall H:C ratio (including the C and H content of the hydrocarbon feed) was the same in the two tests. The experiments were 30 min long. Liquid samples were collected from 5 to 30 min. Conversion results were based on liquid product gas chromatographic analyses. We used a 300 ft long, 0.01-inch ID capillary column coated with Ucon 550-X polypropylene glycol.

Catalysts

Platinum (2%) impregnated on desiccant-grade Davison silica gel (800 m²/g BET surface area). Catalyst preparation was described earlier (1).

Chromia-alumina, containing 0.1% potassium. This catalyst was described in one of our earlier studies (2).

White TCC beads commercial silica-alumina cracking catalyst, manufactured by Socony Mobil Oil Company.

American Cyanamid Aeroextrudate 9999 alumina.

American Cyanamid alumina impregnated with 0.3% lithium (0.43 mmole of lithium per gram catalyst).

American Cyanamid alumina impregnated with 1% sodium (0.43 mmole of sodium per gram catalyst).

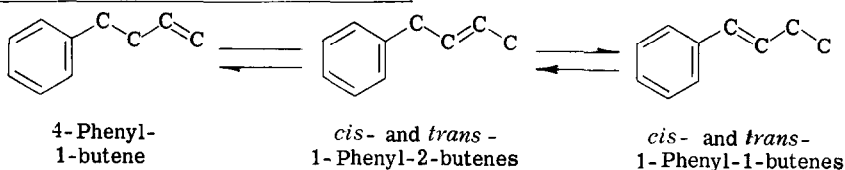
American Cyanamid alumina impregnated with 1% sodium and 3.4% potassium. It contained 0.43 mmole sodium and 0.87 mmole potassium per gram catalyst.

Thermal reactions and reactions catalyzed by the stainless steel reactor were determined in a blank test made using a reactor filled with alundum, an inactive form of α -alumina. Conversion in this test was 1%.

RESULTS

Double-Bond Isomerization

Double-bond isomerization produces *cis*- and *trans*-1-phenyl-1-butenes and 1-phenyl-2-butenes from 4-phenyl-1-butene. The reaction reaches equilibrium distribution (at 371°C, 9% *cis*, plus 59.5% *trans*-1-phenyl-1-butenes, and 9.5% *cis*-, plus



22% *trans*-1-phenyl-2-butenes; at 427°C, the distribution is 10%, 58%, 11%, and 21%) (2) over the pure alumina, silica-alumina, and over the platinum on silica gel catalysts. Since a small amount of feed may go through the reactor without any contact with the catalyst ("channeling"), the equilibrium concentration of 4-phenyl-1-butene among the 1-phenylbutenes is undeterminable. It is probably below 1% (2).

A blank experiment shows less than 1% double-bond isomerization due to reactor-

wall catalysis or thermal reactions at 371°C (Table 1, Experiment No. 1).

Double-bond isomerization may be catalyzed by acids, metals, and alkali metal cations. Neutralization of the catalyst acidity reduces the rate of double-bond isomerization. The rate is decreased more by sodium than by lithium. (The same amount—0.43 mmole alkali metal per gram alumina—is used in each case.) The stronger base (sodium) can neutralize catalyst acidity more effectively than a weaker base. However, alkali metals may also catalyze double-bond isomerization.

Isomerization over the sodium-impregnated alumina with an additional 3.4% potassium (0.87 mmole/g) is significantly higher (Experiment No. 6, Table 1) than over the alumina containing sodium (or lithium) alone.

The equilibrium concentration of 1-phenyl-1-butenes is about 70% of the 1-phenylbutenes (2). At low double-bond isomerization conversions, the concentrations of 1-phenyl-1-butenes is far from this equilibrium level (Experiments 1, 4, and 5, Table 2). This suggests a stepwise reaction mechanism:

The *cis/trans* ratios correspond to equilibrium ratios determined earlier (2).

Double-bond isomerization is catalyzed by hydrogenation-dehydrogenation catalysts also, such as chromia-alumina and platinum (Experiments No. 9, 10, and 11, Table 1).

Skeletal Isomerization

Skeletal isomerization involves the rearrangement of the side chain. 2-Methylphenylpropenes and 2-phenylbutenes are produced

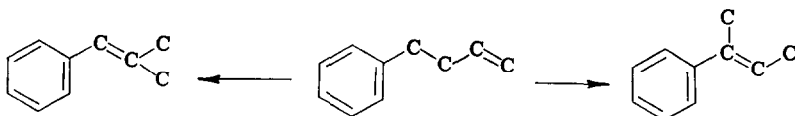


TABLE 1
REACTIONS OF 4-PHENYL-1-BUTENE OVER DIFFERENT CATALYSTS^a

Catalyst: Millimole alkali metal/g catalyst: Experiment number, °C): Reaction temperature, °C): Reaction products, moles/100 moles of feed	Alumina		0.3% Li on Alumina	1% Na on Alumina	1% Na and 3.4% K on Alumina	Silica- alumina	Chromia- alumina	Platinum (2%) on Silica Gel			
	Alundum (cr- alumina)	Alumina	0.43 on Alumina	0.43 on Alumina	1.3 on Alumina	8	9	10			
	371	371	371	371	371	371	371	371			
4-Phenyl-1-butene	99.00	3.62	4.00	32.20	67.80	9.60	5.80	3.14	3.48	0.07	0.37
1-Phenyl-1, and -2-butenes	0.80	91.10	81.20	66.40	31.10	89.30	92.00	14.75	52.18	0.78	2.26
2-Phenylbutenes	0.02	1.65	6.52	0.04	0.01	0.02	0.03	1.83	—	—	—
2-Methyl-1-phenyl-1-propene	—	1.44	4.65	—	—	—	—	2.05	—	—	0.02
Phenylbutadienes	0.01	0.34	0.31	0.25	0.20	0.28	0.28	0.38	0.18	—	—
<i>n</i> -Butylbenzene	0.06	0.96	0.92	0.40	0.37	0.21	0.46	16.95	43.36	94.10	76.20
Isobutylbenzene	—	—	—	—	—	—	—	0.61	—	0.16	0.30
<i>sec</i> -Butylbenzene	—	0.04	0.06	—	—	—	—	3.45	—	—	0.33
1-Methylindan	0.04	0.28	0.93	0.40	0.26	0.25	0.70	47.70	0.33	2.35	6.57
1-Methylindene	0.006	0.06	0.27	0.03	0.01	0.01	0.07	3.28	—	0.20	2.46
3-Methylindene	—	0.007	0.02	—	—	—	0.01	0.40	—	0.02	0.28
2-Methylindan and 2-methylindene	—	0.004	0.04	—	—	—	—	1.32	—	0.004	0.29
Tetralin	—	0.05	0.29	0.015	0.005	0.005	0.004	0.59	—	0.002	0.005
Naphthalene	—	—	0.03	0.004	0.003	0.003	0.024	0.13	—	1.26	8.20
Benzene	0.002	0.01	0.07	0.01	0.01	0.03	0.07	1.67	0.01	0.22	0.40
Toluene	0.01	0.03	0.14	0.08	0.05	0.10	0.20	0.40	0.04	0.24	0.76
Ethylbenzene	0.002	0.01	0.02	0.005	0.004	0.01	0.02	0.36	0.02	0.26	0.89
Styrene	0.02	0.17	0.27	0.07	0.04	0.04	0.07	0.03	0.003	—	—
<i>n</i> -Propylbenzene	0.001	0.002	0.002	0.003	0.001	0.001	0.002	0.05	0.004	0.33	0.66
C ₁₁ and higher aromatics	—	—	—	—	—	—	—	0.74	—	—	—
Other	0.03	0.23	0.26	0.09	0.14	0.14	0.26	0.17	0.39	—	—
Methane	—	—	0.01	—	—	—	0.005	0.16	—	0.14	0.87
Ethane, ethylene	0.002	0.05	0.05	0.01	0.004	0.007	0.03	2.11	—	0.11	0.90
Propane, propylene	0.002	0.19	0.20	0.03	0.01	0.01	0.05	0.12	—	0.08	0.39
Butane	—	—	—	—	—	—	—	1.22	—	0.04	0.19
Butenes	—	0.01	0.02	—	—	—	—	0.19	—	—	0.03

^a Reaction conditions: Atmospheric total pressure, an LHSV of 6.8, and an initial H₂-to-feed molar ratio of 4. The runs were 30 min long. Liquid products were collected from the 5th to the 30th min. Results of liquid product analyses.

These may later be hydrogenated to isobutylbenzene and *sec*-butylbenzene. Acids are good catalysts for skeletal isomerization. The reaction is most extensive over silica-alumina. Alkali metal addition to alumina almost completely stops skeletal isomerization. The conversion drops from 11% to 0.04% after the alumina has been impregnated with 0.3% lithium (Table 2).

Isomerization proceeds over the neutral platinum on silica gel catalyst by different mechanisms: *sec*-butylbenzene is formed via cyclic intermediates and a non-carbonium ion-type 1,2-methyl shift forms isobutylbenzene.

Cyclization

1-Phenylbutenes may form five- or six-membered rings (i.e., 1-methylindan or tetralin) by cyclization. These in turn may dehydrogenate, yielding methylindenes or naphthalene. Over acidic catalysts 1-methylindan and -indenes may isomerize to 2-methylindan or -indene.

Our work with *n*-butylbenzene (1) revealed two cyclization mechanisms, one catalyzed by acid sites, the other by the platinum metal. Over platinum on silica gel, only the platinum-catalyzed reaction occurs. Cyclization by this mechanism produces nearly equal amounts of five- and six-membered ring products (i.e., methylindan and naphthalene). Cyclization of phenylbutenes over the platinum on silica gel catalyst almost exactly parallels that of *n*-butylbenzene (Table 3). Since rapid hydrogenation of the phenylbutenes results in about the same *n*-butylbenzene/phenylbutene ratio as observed with the *n*-butylbenzene feed, this is hardly unexpected.

Over silica-alumina and the alumina catalysts cyclization proceeds by an acid-catalyzed self-alkylation mechanism. This reaction involves an attack by an electron-deficient carbon atom of the side chain on the aromatic ring. The stability of the intermediate carbonium ion determines whether five- or six-membered rings will be formed. Formation of six-membered

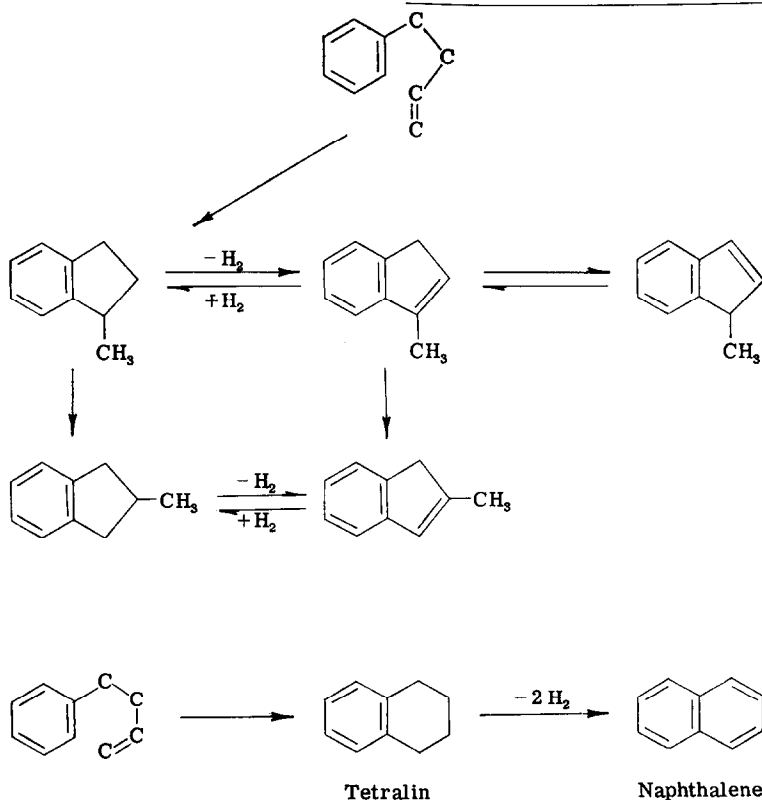


TABLE 2
 ISOMERIZATION OF 4-PHENYL-1-BUTENE AT 371°C

Catalyst	Experiment No.	Double-bond isomerization			Skeletal isomerization		
		Isomerized olefins		1-Phenyl-1-butenes, % of isomerized olefins	2-Phenylbutenes and 2-methyl-1-phenylpropenes		<i>sec</i> -Butyl- and isobutylbenzene Moles per 100 moles of feed
		Total conversion (mole %)	% of total phenylbutenes		Moles per 100 moles of feed	% of total phenylbutenes	
Alundum	1	0.8	0.8	29	0.02	0.02	—
Alumina	3	81.2	95.3	69	11.2	11.6	0.06
Li (0.3%) ^a on alumina	4	66.4	67.3	44	0.04	0.04	—
Na (1%) ^a on alumina	5	31.1	32.5	58	0.01	0.01	—
Na (1%) + K (3.4%) on alumina	6	89.3	90.3	68	0.02	0.02	—
Silica-alumina	8	14.8	^b	70	3.9	17.8	4.1
Pt (2%) on silica gel	10	0.8	^b	73	0	0	0.16

^a 0.43 millimole alkali metal/g catalyst.

^b Not determined because figure would be meaningless due to the channeling of feed.

rings (tetralin or naphthalene) from *n*-butylbenzene or 1-phenylbutenes would involve a very unstable primary carbonium ion. Thus, acid-catalyzed cyclization produces almost exclusively methylindan and methylindenes from *n*-butylbenzene or phenylbutenes. Hence, the large difference between the (methylindans + methylindenes)/(tetralin + naphthalene) ratios

observed over silica-alumina and platinum-silica gel catalysts (73 versus 2 at 371°C, Table 4). Tetralin \rightleftharpoons methylindan isomerization is negligible under these conditions (3).

The phenylbutene experiments confirm the mechanism reported earlier (1) for acid-catalyzed cyclization. This mechanism involves carbonium ion $C_6H_5CH_2CH_2C^+HCH_3$.

 TABLE 3
 COMPARISON OF *n*-BUTYLBENZENE AND 4-PHENYL-1-BUTENE FEEDS
 OVER PLATINUM-SILICA GEL AND SILICA-ALUMINA CATALYSTS

Catalyst:	2% Platinum on silica gel		Silica-alumina	
	Reaction temperature (°C): Feed:		427°	371°
Product composition, moles/100 moles of feed	<i>n</i> -Butylbenzene	4-Phenyl-1-butene	<i>n</i> -Butylbenzene	4-Phenyl-1-butene
1-Phenyl-1, and -2-butenes	2.0	2.26	0	14.8
1-Methylindan + Methylindenes	10.9	9.3	0.15	51.4
Naphthalene + tetralin	11.9	8.2	0	0.7
Isobutylbenzene + methylphenylpropene	0.36	0.32	0.01	2.7
<i>sec</i> -Butylbenzene + 2-phenylbutenes	0.31	0.33	0.05	5.3
C ₆ —C ₉ aromatics	4.1	2.7	1.9	2.5
Methylindan + methylindenes	0.9	1.2	∞	73
Naphthalene + tetralin	—	—	—	—
1-Methylindan/methylindenes	2.8	2.4	∞	13
Tetralin/naphthalene	—	0.0006	—	4.5
Distribution of fragmentation products, mole % of total fragmentation				
Phenyl- α C—C Bond Broken	15	15	99.1	67
α - β C—C Bond Broken	27	28	0.5	16
β - γ C—C Bond Broken	33	33	0.25	15
γ - δ C—C Bond Broken	25	24	0.15	2

TABLE 4
 CYCLIZATION OF 4-PHENYL-1-BUTENE OVER DIFFERENT CATALYSTS

Catalyst	Tem- pera- ture (°C)	Total cy- clization, moles/ 100 moles of feed	Methylindan + methylindenes	1-Methylindan	Tetralin
			Naphthalene + tetralin	1-methylindenes	naphthalene
Silica-alumina	371°	53.4	73	13	4.5
Alumina	316°	0.40	7	4	∞
Alumina	371°	1.58	4	3	10
Alumina + 0.43 mmole/g Li	371°	0.45	23	13	4
Alumina + 0.43 mmole/g Na	371°	0.28	34	26	2
Alumina + 1.3 mmole/g (Na + K)	371°	0.27	33	25	2
Alumina + 1.3 mmole/g (Na + K)	427°	0.81	28	9	0.2
Platinum on silica gel	371°	3.84	2	11	0.0016
Platinum on silica gel	427°	17.80	1.2	2.4	0.0006

This may be produced by phenylbutene protonation, or by hydride abstraction from *n*-butylbenzene. Over silica-alumina, dehydrogenation of *n*-butylbenzene is very slow. Phenylbutenes are not present in the reaction product (Table 3). Dehydrogenation to phenylbutenes might be the rate-controlling step in *n*-butylbenzene cyclization, unless the carbonium ion intermediate is formed by hydride abstraction. Cyclization of phenylbutenes at 371°C is more than 340 times faster than that of *n*-butylbenzene at 427°C (Table 3). Thus, cyclization rates of *n*-butylbenzene and 4-phenyl-1-butene may differ by as much as a factor of 2000. Protonation of the double bond might be the predominant way of carbonium ion formation over silica-alumina. With phenylbutene feed, dehydrogenation is no longer rate-controlling; hence, the large difference in reactivity.

The rate of cyclization is substantially slower over alumina than over silica-alumina. Alkali metal addition reduces the rate of cyclization. Cyclization to six-membered rings is affected more than cyclization to five-membered rings (Tables 1 and 4). Sodium has a stronger effect than lithium. Addition of 0.9 mmole potassium/g to alumina containing 0.4 mmole sodium/g does not reduce cyclization rates any further. This slow, residual cyclization may not be acid-catalyzed.

Over the acidic catalysts, and to some extent over platinum on silica gel, 1-methylindan and 1-methylindene may

isomerize to 2-methylindan and 2-methylindene (Table 1).

Hydrogenation-Dehydrogenation

Hydrogenation is very fast over platinum-on-silica gel. The 1-phenylbutenes/*n*-butylbenzene ratios are about equal whether the feed is *n*-butylbenzene with an H₂:feed ratio of 3, or 4-phenyl-1-butene with an H₂:feed ratio of 4 (0.0285 and 0.0295 at 427°C). This ratio represents equilibrium between the 1-phenylbutenes and *n*-butylbenzene. The rate is substantially slower over chromia-alumina: Less than half of the phenylbutenes are hydrogenated (Experiment 9, Table 1). Hydrogenation is very slow over the alumina catalysts. Alkali metal impregnation further decreases hydrogenation. Silica-alumina has higher hydrogenation activity than alumina. Olefins with a tertiary carbon atom are hydrogenated preferentially over silica-alumina; the *sec*-butylbenzene/2-phenylbutenes ratio is higher than the *n*-butylbenzenes/1-phenylbutenes ratio (1.9 versus 1.1). Dehydrogenation produces phenylbutadienes (about 0.2%) over all the oxide catalysts.

Hydrogenation and dehydrogenation of bicyclic hydrocarbons is very fast over platinum on silica gel. Tetralin and naphthalene are at equilibrium with each other (Table 4). The same is true for 1-methylindan and the methylindenes. Dehydrogenation is very slow over the alumina and silica-alumina catalysts. The tetralin/

TABLE 5
FRAGMENTATION OF 4-PHENYL-1-BUTENE OVER ALUMINA AND SILICA-ALUMINA CATALYSTS
DISTRIBUTION OF PRODUCTS, AS PERCENT OF TOTAL FRAGMENTATION

Catalyst:		Alumina		0.3% Li on alumina	1% Na on alumina	1% Na + 3.4% K on alumina		Silica Alumina
Temperature (°C): Experiment:		316°	371°	371°	371°	371°	427°	371°
Position	Products of fragmentation	2	3	4	5	6	7	8
Phenyl- α	Benzene + butane, butenes	5	14	6	9	16	19	67
α - β	Toluene + propane, propylene	13	28	48	48	55	55	16
β - γ	Ethylbenzene, styrene + ethane, ethylene	81	57	44	42	28	25	15
γ - δ	<i>n</i> -Propylbenzene β -methylstyrenes, + methane	1	1	2	1	1	1	2
Total fragmentation products, mole % of feed		0.22	0.50	0.17	0.11	0.18	0.36	2.51

naphthalene ratio is substantially higher than the equilibrium value (Table 4). Tetralin is the primary six-membered ring cyclization product over acid catalysts. Naphthalene is produced in a consecutive step.

Fragmentation

There are two catalytic fragmentation procedures: hydrogenolysis and cracking. A molecule of hydrogen is added in hydrogenolysis and no new unsaturated bond is formed. In cracking one of the fragments is formed with an additional unsaturated bond. However, in the presence of a hydrogenation catalyst differentiating between cracking and hydrogenolysis is not always simple. The olefinic cracking products could become saturated, or the paraffinic products of hydrogenolysis may be dehydrogenated.

Fragmentation proceeds exclusively by hydrogenolysis over platinum-silica gel. In hydrogenolysis, the different side chain bonds of an alkylaromatic have about equal scission probabilities (1). Since the rate of hydrogenation of phenylbutenes is very much faster than hydrogenolysis, 4-phenyl-1-butene and *n*-butylbenzene have identical fragmentation patterns (Table 3).

Cracking is the only type of fragmentation over silica-alumina. With *n*-butylbenzene, over 99% of the cracking occurs between the phenyl ring and the α -carbon atom of the side chain (Table 3). The cracking pattern of 1-phenylbutenes is dif-

ferent (Table 5). Phenyl- α scission is only 67% of the total fragmentation. Scissions to styrene plus ethylene and toluene plus a C₃ hydrocarbon also occur.

Overall fragmentation over the alkali metal-poisoned aluminas is very low. The pattern of fragmentation differs from either acid-type cracking or metal-catalyzed hydrogenolysis. The abundance of toluene among the fragmentation products suggests a radical mechanism. Over the pure alumina, scission to styrene and ethylene prevails (Table 5). The poisoning of this reaction by alkali metals suggests acid-type catalysis. The acidity of alumina is not strong enough to promote the scission of the phenyl- α bond.

CONCLUSIONS

Over silica-alumina the rate of cyclization of 4-phenyl-1-butene is about 2000 times higher than that of *n*-butylbenzene. Methylindan is the product in both cases. This reconfirms the mechanism proposed (1) for the acid-catalyzed cyclization of alkylbenzenes, a self-alkylation process involving carbonium ion intermediates. The preferred way of carbonium ion formation over silica-alumina is protonation of olefinic bonds. Hydride abstraction is unimportant compared to double-bond protonation. In the absence of a dehydrogenation component (such as in the case of pure silica-alumina), formation of phenylalkenes from alkylbenzenes is very slow. Thus, de-

hydrogenation becomes the rate-controlling step of the cyclization of alkylbenzenes.

Alumina has lower cyclization activity than silica-alumina. Alkali metal addition further decreases this activity. A slow, nonacid-type cyclization mechanism may also operate over alumina catalysts.

Over platinum on silica gel the rate of hydrogenation of the phenylbutenes is very much faster than any of the other reactions. Reaction rates and selectivities of 4-phenyl-1-butene and *n*-butylbenzene are therefore very similar. For example, cyclization rates are almost identical, and distribution of the products of hydrogenolysis are the same.

Double-bond isomerization may be catalyzed by acids, bases, or metals. Over acidic and basic catalysts the reaction occurs stepwise. Thermal isomerization at our reaction conditions is very slow. Skeletal isomerization of the side chain is mostly acid-catalyzed.

Acid-catalyzed cracking of the unsatu-

rated side chain differs from cracking of a saturated side chain. Besides splitting the bond between the phenyl ring and the α -carbon of the side chain, other processes—such as splitting to styrene and ethylene—also occur. Toluene formation over the alkali metal-poisoned aluminas suggests free-radical type cracking.

Hydrogenation is very fast over platinum, fast over chromia-alumina, moderate over silica-alumina, and very slow over alumina. Alkali metals further decrease the hydrogenation activity of alumina.

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