Production of Branched Alkanes by Acid-Catalyzed Dealkylation of Linear Alkylbenzenes[1]

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Received February 14, 1978

The dealkylation of several secondary butyl-, pentyl-, and hexylbenzenes produced by heating them with $AlCl_3$, Al_2Br_6, and $HF{\cdot}SbF_5$ has been studied. The major alkane from 2-phenylbutane was *n*-butane (72%), whereas the major alkanes from 2- or 3-phenylpentane and 2- or 3-phenylhexane were the branched isomers (90–97%). Addition of a hydride ion donor such as methylcyclopentane or methylcyclohexane increased the proportion of *n*-alkane, and dilution of the alkylbenzene with benzene decreased the proportion of *n*-alkane. These results are rationalized in terms of initial cleavage of the alkyl group as a secondary carbocation, followed by hydride donation from the side chain of a second alkylbenzene molecule or an added hydride donor. The enormous difference in the extent of formation of branched alkanes from the butylbenzene and from the higher homologues is attributed to the ability of the carbocations from the latter to rearrange via protonated cyclopropane intermediates and thereby avoid primary carbocation intermediates, whereas the butyl carbocations cannot rearrange except via the higher energy forms.

In 1963, we reported a study of the dealkylation of a number of alkylbenzenes with side chains of 2–5 carbon atoms, using water-activated aluminum chloride as catalyst.[2] In this study, we confirmed that the ease of dealkylation was in the order of tertiary > secondary > primary alkyl, as reported by Ipatieff and Pines,[3] and we showed that the addition of a special hydride donor such as methylcyclopentane was unnecessary.

In reconsidering our dealkylation data recently, an aspect which intrigued us was the difference in the proportions of normal and branched alkanes produced by 2-phenylbutane (*sec*-butylbenzene) and 2-phenylpentane. The major product from 2-phenylbutane was *n*-butane (70%), whereas 2-phenylpentane gave only 4% *n*-pentane and 96% isopentane. We decided to repeat some of the earlier experiments on butyl- and pentylbenzenes in order to check them carefully and to extend the work to the hexylbenzenes.

In the interim, several reports of related work have appeared. Trapping of the *tert*-butyl cation produced by dealkylation of *tert*-butylarenes with carbon monoxide and boron trifluoride hydrate to give pivalic acid was described.[4] NMR evidence of dealkylative formation of the *tert*-butyl cation from protonated alkylbenzenes in superacid media at low temperatures was reported by Olah and co-workers.[5] The formation of a mixture of branched alkanes was observed to accompany the alkylation of benzene with *n*-octyl and *n*-dodecyl bromides and aluminum bromide.[6] The dealkylation and transalkylation reactions of a number of alkylbenzenes induced by aluminum chloride were investigated by Ogawa and co-workers.[7] They reported that dealkylation of *sec*-butylbenzene produced *n*-butane, but isobutylbenzene gave isobutane, and all of the pentylbenzenes except *n*-pentylbenzene gave isopentane.[7a]

Results and Discussion

The results of the new work on butyl- and pentylbenzenes are summarized in Tables I and II. Runs 1 and 3 duplicated experiments reported earlier[2] on 2-phenylbutane (*sec*-butylbenzene) and 2-phenylpentane, and the results were the same as before. In the earlier study, we determined the proportion of *n*-butane and isobutane produced from both *sec*-butylbenzene and isobutylbenzene with short reaction times at 100 °C.[2] We found that the first gas evolved (10–12 s) when butylbenzene was dropped onto the hot aluminum chloride was mainly isobutane.

We concluded that both *sec*-butyl- and isobutylbenzene rapidly isomerized to *tert*-butylbenzene when first mixed with the hot catalyst, and the *tert*-butylbenzene produced immediately underwent dealkylation. The slow evolution of butanes which occurred after the first 15–20 min was considered to represent the direct dealkylation of *sec*-butyl- and isobutylbenzene by the deactivated catalyst, in about 2:1 ratio, as would be expected. No *tert*-butylbenzene was found in the liquid reaction mixtures, but this was not surprising in view of its known greater susceptibility to dealkylation and fragmentation reactions than the other butylbenzene isomers. A similar explanation was given for the fact that the major alkane evolved from all pentylbenzenes was isopentane.

In the present study, possible changes with time in the ratio of isopentane/*n*-pentane from 2-phenylpentane at 100 °C were carefully investigated, but no change was found between 2 min and 3 h. It was also found that the ratio of isopentane to *n*-pentane did not vary with the duration of time at lower temperatures (60 and 75 °C). In other work reported in 1963, we found that when *tert*-pentylbenzene underwent aluminum chloride catalyzed dealkylation, at the same time it isomerized rapidly to 2-methyl-3-phenylbutane and more slowly to neopentylbenzene.[8] In the present experiments, no *tert*-pentylbenzene, 2-methyl-3-phenylbutane, or neopentylbenzene could be detected in the liquid mixtures from 2- or 3-phenylpentane. Under very mild conditions (at 30 °C) the dealkylation product of 2-phenylpentane was entirely isopentane; no *tert*-pentylbenzene was observed in the liquid reaction mixture, nor was any 2-methyl-3-phenylbutane or neopentylbenzene detected. The only pentylbenzene isomers observed were 3-phenylpentane and 2-methyl-1-phenylbutane (run 4, Tables I and II), in accordance with the previous reports from this laboratory.[2] These results led us to doubt that *tert*-pentylbenzene is the intermediate leading to isopentane.

Although there are no analogous arguments to rule out *tert*-butylbenzene as the intermediate leading to isobutane production in the early stages of the dealkylation of *sec*-butylbenzene and isobutylbenzene, the fact that rearrangement of *sec*-butylbenzene and isobutylbenzene to *tert*-butylbenzene would appear to require the same kinds of carbocation intermediates as the rearrangements of 2-phenylpentane and 2-methyl-1-phenylbutane to *tert*-pentylbenzene led us to question our earlier conclusion that *tert*-butylbenzene was an intermediate in the dealkylations of *sec*-butylbenzene and isobutylbenzene.

In 1968 Brouwer and Oelderik observed that *n*-pentane was isomerized to isopentane by $HF–SbF_5$, but *n*-butane was not isomerized to isobutane under the same conditions.[9] Soon after this, Kramer[10] demonstrated that the secondary carbocation produced from 2-chlorobutane in $HSO_3F–SbF_5$ could

0022-3263/78/1943-2977$01.00/0

Table I. Gaseous Dealkylation Products from Secondary Butyl- and Pentylbenzenes[a]

Run no.	1	2	3	4	5	6	7
Alkylbenzene	2-PB[b]	2-PB[b]	2-PP[c]	2-PP[c]	2-PP[c]	3-PP[d]	3-PP[d]
Solvent (mol)		MCH[e] (0.6)			MCH[e] (1.2)		MCH[e] (1.2)
Reaction temp, °C	100	100	100	30	80	80	80
Mol % dealkylation[f]	31	48	21	1	8	14	7
Alkane distribution,[g] %							
n-C_4H_{10}	72	89					
i-C_4H_{10}	27	11	Trace				
n-C_5H_{12}			4	Trace	16	3	19
i-C_5H_{12}	1		96	100	84	97	81

[a] Mole ratio of reactants, R-C_6H_5/$AlCl_3$/H_2O = 1.0:0.33:0.11; reaction time, 3 h. [b] 2-Phenylbutane. [c] 2-Phenylpentane. [d] 3-Phenylpentane. [e] Methylcyclohexane. [f] Mol % conversion to alkanes based on alkylbenzene and calculated from volume of gas collected. [g] GLC analysis.

Table II. Liquid Dealkylation and Fragmentation Products from Secondary Butyl- and Pentylbenzenes[a]

Run no.	1	3	4	5	6	7
Alkylbenzene	2-PB	2-PP	2-PP	2-PP	3-PP	3-PP
Product total,[b] %	27	21	68	17	38	15
C_6H_5-R,[c] mol %						
Me	4	2				Trace
Et	13	12		1	1	2
n-Pr	3	1				
i-Pr	5	10		1	1	1
sec-Bu	26			Trace	Trace	Trace
i-Bu	49	Trace		Trace	Trace	Trace
n-Bu				4		2
2-Pe[d]		37	56	42	53	46
3-Pe		11	33	10	12	12
2-MB[e]		27	11	42	33	37

[a] Conditions, reactants, and run numbers are the same as in Table I. [b] Weight % of original alkylbenzene of products; bp 80–220 °C. [c] Mol % of the alkylbenzenes from GLC analysis. [d] 2-Pentyl. [e] 2-Methyl-1-butyl.

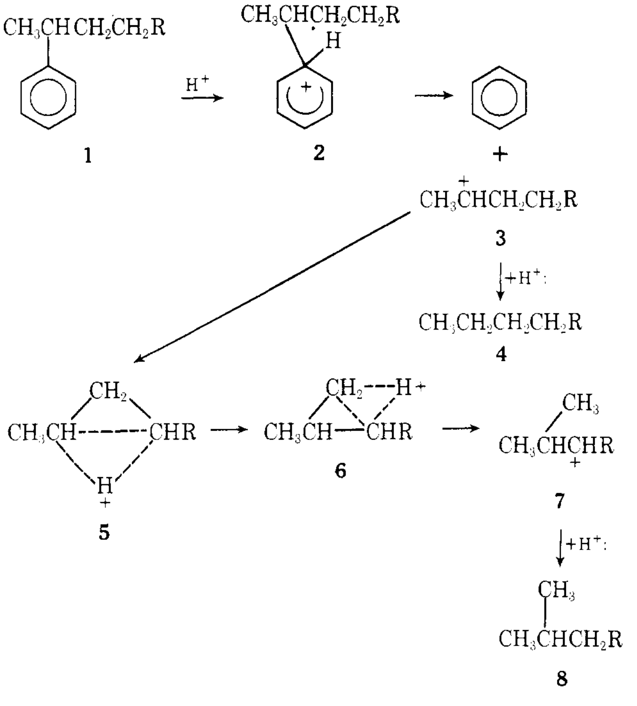
be trapped by a hydride donor before rearrangement to the tertiary carbocation much more successfully than the corresponding secondary carbocation from 2-chloropentane; i.e., the tendency of the secondary *pentyl* carbocation to rearrange was much greater than that of the *butyl* carbocation. The principle proposed by Brouwer and Oelderik to rationalize their observations of alkane isomerizations, and which was applied by Kramer to explain his results, was that carbocation isomerizations such as these, which involve a change in the degree of branching, pass through protonated cyclopropane intermediates. The significant difference in the behavior of butyl and pentyl systems can be rationalized in terms of the ability of the pentyl intermediates thus to avoid primary carbocation character, whereas butyl intermediates cannot.

It occurred to us that this principle might also be applied to explain the difference in the amount of branched alkanes produced from dealkylation of butyl- and pentylbenzenes. Referring to Scheme I, one may see that in the case of 2-phenylbutane (**1a**), the carbocation intermediate **7a** formed by the opening of the protonated cyclopropane intermediate **6a** would have primary carbocation character, whereas the corresponding intermediate (**7b**) from 2-phenylpentane (**1b**) would have secondary carbocation character. Assuming that the capture of the initial secondary carbocation **3** by a hydride ion is competitive with its rearrangement to **7** via **5** and **6**, increasing the concentration of potential hydride donors in the reaction medium should increase the proportion of *n*-alkane to isoalkane.

In run 2 (Table I) it may be seen that addition of methylcyclopentane to 2-phenylbutane increased the proportion of *n*-butane from 72 to 89% in the mixture of butane isomers produced. Similarly, the proportion of *n*-pentane from 2-phenylpentane was increased from 4 (run 3) to 16% (run 5) by the addition of methylcyclohexane, and a slightly larger increase (from 3 to 19%) was produced from 3-phenylpentane (runs 6 and 7).

Hexylbenzenes. Results from dealkylations of three secondary hexylbenzenes are presented in Table III. Heating either 2- or 3-phenylhexane with Al_2Br_6 at 80 °C gave 2-methylpentane, 3-methylpentane, and *n*-hexane in ratios of

Scheme I



a, R = H; b, R = CH_3

Table III. Dealkylation of Secondary Hexylbenzenes

Run no.[a]	Hexylbenzene	Catalysts	Solvents	Temp, °C	Time, h	Dealkylation,[b] mol %	Distribution of alkanes, %		
							2-MP[c]	3-MP[d]	H[e]
17	2-PH[f] (0.1)[g]	Al_2Br_6 (0.033)		80	3	19	53	37	10
18		Al_2Br_6 (0.033)		80	3	19	52	38	10
19		Al_2Br_6 (0.033) HBr (0.02)		80	3	38	56	37	7
20		Al_2Br_6 (0.033) HBr (0.02)		55	3	36	57	35	8
21		Al_2Br_6 (0.033) HBr (0.059)	PhH (4.9)	35	1	52	65	35	
22		Al_2Br_6 (0.023)	PhH (4.9)	35	1	11	77	23	
23		Al_2Br_6 (0.023) HBr (0.062)	PhH (4.9)	65	1	54	70	30	
24		Al_2Br_6 (0.023) HBr (0.065)	PhH (4.9) MCH[h] (1.2)	70	2	70	59	27	14
25		Al_2Br_6 (0.023) HBr (0.167)	PhH (4.9)	70	2	63	68	32	
26		Al_2Br_6 (0.033) HBr (0.065)	PhH (4.9)	70	1	60	69	31	
27		Al_2Br_6 (0.033) HBr (0.065)	PhH (4.9) MCH (1.2)	35	2	65	59	27	14
28		Al_2Br_6 (0.033) HBr (0.065)	PhH (4.9) MCH (1.2)	65	2	73	61	25	14
29	3-PH[i] (0.1)	Al_2Br_6 (0.033)		80	2		50	34	16
30		Al_2Br_6 (0.033)	PhH (4.9)	35	2	32	67	33	
31	3-PH (0.1)	Al_2Br_6 (0.033)	PhH (4.9)	80	2	51	67	33	
32		Al_2Br_6 (0.033) HBr (0.1)	PhH (4.9) MCH (0.6)	80	2	84	60	30	10
33		Al_2Br_6 (0.033)	PhH (4.9)	70	2	62	69	31	
34	3-M-2-PP[j] (0.025)	Al_2Br_6 (0.008)	MCP[k] (0.3)	35	2	33	30	70	
35		Al_2Br_6 (0.004)	CH[l] (0.357)	35	2	24	69	31	

[a] Runs 17–20 and 29 were carried out by procedure A (see Experimental Section); all other runs were carried out by procedure B. [b] Based on hexylbenzenes and calculated from GLC analysis with an internal standard. [c] 2-Methylpentane. [d] 3-Methylpentane. [e] *n*-Hexane. [f] 2-Phenylhexane. [g] Numbers in parentheses are molar quantities. [h] Methylcyclohexane. [i] 3-Phenylhexane. [j] 3-Methyl-2-phenylpentane. [k] Methylcyclopentane. [l] Cyclohexane.

50–52:34–38:10–16%, respectively (runs 17, 18, and 29). The addition of HBr increased the yield of dealkylation without changing the proportion of alkane isomers (run 19). When the reaction was carried out in benzene solution, however, none of the unbranched alkane isomer could be detected (runs 21–23, 25, 26, 31, and 33). This is puzzling at first, but when one considers the source of the hydrogen which traps the secondary hexyl cation before rearrangement to convert it to *n*-hexane, a reasonable explanation emerges. It is the 2- or 3-phenylhexane itself which can donate a tertiary hydrogen from its side chain. When the reaction is carried out in benzene solution, the concentration of this hydride donor is much reduced by the dilution in benzene, and the secondary hexyl cation rearranges before it can acquire a hydrogen. This assumption is supported by the results from the experiments in which an additional hydride donor, methylcyclohexane or methylcyclopentane, was added as well as benzene (runs 24, 27, 28, and 32); in all of these experiments *n*-hexane was observed, and the overall yield of dealkylation was also increased.

The results from the studies of dealkylation of 3-methyl-2-phenylpentane also fit this picture. When the reaction was carried out in cyclohexane solution (run 35), the ratio of 3-methylpentane to 2-methylpentane was 31:69, essentially the equilibrium proportion of these isomers. However, when the solvent was methylcyclopentane (run 34), the ratio of isomeric methylpentanes was reversed, owing to the ability of the better hydride donor to trap some of the 3-methyl-2-pentyl cations before the methyl shift occurred.

Alkane Formation Accompanying Alkylations with Secondary Hexyl Bromides. The observation by Sharman[6] of branched alkanes as byproducts of the alkylation of benzene with *n*-octyl and *n*-dodecyl bromides was mentioned earlier. The "branched alkanes" were not identified further. They were said to arise from dealkylation of the secondary alkylbenzenes, whereas the primary alkylbenzenes were stable to the reaction conditions. This report led us to carry out some alkylations with 2- and 3-bromohexanes in order to compare the six-carbon system with the eight- and twelve-carbon systems of Sharman, with the expectation that the isomeric hexanes could be identified easily.

The results of these reactions are presented in Table IV. The experimental conditions of runs 8 and 16 correspond to those of Sharman's experiment A.[6] The yields of dealkylation products were about the same as he reported for the reaction of 1-bromododecane. Our products were 2- and 3-methylpentane; in about the same proportion they were produced by dealkylation of 2- and 3-phenylhexane (Table III). Increasing the mole ratio of aluminum bromide/bromohexane increased the extent of dealkylation: compare run 8 with 11 and run 16 with 15. The addition of hydrogen bromide to the reaction mixture also increased the extent of dealkylation: compare runs 11 and 9. As was found in the dealkylations carried out in benzene solution, no *n*-hexane was observed except when a good hydride donor was added, such as methylcyclopentane (run 10) or methylcyclohexane (run 14).

2- and 3-bromohexanes gave almost identical yields of dealkylation and proportions of 2- and 3-methylpentanes. The equilibration probably occurs at the phenylhexane stage. In an alkylation with 3-bromohexane at −5 °C, when samples were withdrawn before the reaction was complete, no isomerization of 3-bromohexane to 2-bromohexane had occurred. This finding was in agreement with Sharman's report that recovered octyl and dodecyl bromides showed no rearrange-

Table IV. Alkylation-Dealkylation with Bromohexanes[a]

Run no.	Bromohexane	Catalysts	Solvents	Temp, °C	Dealkylation,[b] mol %	Distribution of alkanes, % 2-MP	3-MP	H
8	2-BH[c] (0.1)[d]	Al_2Br_6 (0.023)	PhH (4.9)	35	51	68	32	
9		Al_2Br_6 (0.033) HBr (0.065)	PhH (4.9)	65	71	69	31	
10		Al_2Br_6 (0.033)	PhH (4.9) MCP[e] (0.5)	65	74	65	27	8
11		Al_2Br_6 (0.033)	PhH (4.9)	65	65	65	35	
12		Al_2Br_6 (0.033)	PhH (4.9)	80	68	66	34	
13	3-BH[f] (0.1)	Al_2Br_6 (0.033)	PhH (4.9)	80	67	68	32	
14		Al_2Br_6 (0.033)	PhH (4.9) MCH[g] (1.2)	80	86	59	26	15
15		Al_2Br_6 (0.033)	PhH (4.9)	35	64	69	31	
16		Al_2Br_6 (0.023)	PhH (4.9)	35	52	70	30	

[a] All of the reaction times were 2 h. [b] Based on bromohexanes and calculated from GLC with an internal standard. [c] 2-Bromohexane. [d] Numbers in parentheses are molar quantities. [e] Methylcyclopentane. [f] 3-Bromohexane. [g] Methylcyclohexane.

Table V. Dealkylation of Secondary Hexylbenzenes with HF–SbF_5[a]

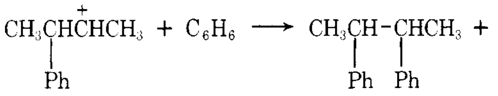
Run no.	Hexylbenzene	Solvent	Temp, °C	Dealkylation,[b] mol %	Distribution of alkanes,[c] % 2,2-DMB	2,3-DMB	2-MP	3-MP	H
36	2-PH[d]	Benzene	80				68	32	
37	3-PH[e]	Benzene	80				68	32	
38	2-PH		80	24	4	18	43	26	9
39	3-PH		80	25	3	17	42	28	10
40	3-PH		35	21	2	19	49	26	4
41	3-PH	MCH[f]	35	36	9	18	42	24	7
42	2-PH		35	22	2	18	49	27	4
43	2-PH	MCH[f]	35	38	8	19	42	25	6

[a] Mole ratio, 2- or 3-phenylhexane/HF–SbF_5/benzene (when present) = 0.025:0.0165:1.2; reaction time, 0.5 h except 2 h for runs 36 and 37. [b] Mol % of dealkylation based on hexylbenzene and calculated from GLC analysis with an internal standard. [c] Abbreviated alkanes: 2,2-dimethylbutane (2,2-DMB); 2,3-dimethylbutane (2,3-DMB); 2-methylpentane (2-MP); 3-methylpentane (3-MP); *n*-hexane (H). [d] 2-Phenylhexane. [e] 3-Phenylhexane. [f] Methylcyclohexane; 0.5 mol/0.05 mol of hexylbenzene.

ments before alkylation,[6] but it contrasts with our earlier observation of isomerization of secondary chloropentanes and chlorohexanes prior to alkylation when aluminum chloride was the catalyst.[11]

Reaction of Hexylbenzenes with HF–SbF_5. Brouwer and Oelderik[9] found that treatment with fluoroantimonic acid produced all of the hexane isomers from 2-methylpentane. The formation of 3-methylpentane was the fastest reaction, followed by the conversion of these two isomers to 2,3-dimethylbutane, while the isomerizations to *n*-hexane and 2,2-dimethylbutane were the slowest reactions. Although we found neither of the doubly branched hexanes as dealkylation products from reaction of 2- or 3-phenylhexane with aluminum bromide, we thought they might be produced in the presence of fluoroantimonic acid. In benzene solution at 80 °C, only 2- and 3-methylpentane were produced, in about the same proportion as with aluminum bromide catalyst (Table V, runs 36 and 37). However, when the fluoroantimonic acid was not diluted by benzene, all five isomeric hexanes were produced, even at 35 °C (runs 38–40). Addition of methylcyclohexane gave a higher yield of dealkylation products and increased the proportion of *n*-hexane and 2,2-dimethylbutane (runs 41 and 43).

Rearrangement and Cyclialkylation Products from Hexylbenzenes. The high-boiling aromatic components of the reaction mixtures were also examined, with the aim of gaining more insight into the mechanism of the dealkylation process and its relationship to other competing or conjugated processes. In our earlier study of dealkylations[2] we identified diphenylalkanes as the probable byproducts resulting from the hydride donation by the alkylbenzenes required to produce the alkanes. In support of this theory, we cited the isolation of *meso*-2,3-diphenylbutane from an aluminum chloride catalyzed dealkylation of *sec*-butylbenzene. The formation of this compound is reasonably explained in terms of the intermediate carbocation **9**, which results from hydride donation to a butyl cation by *sec*-butylbenzene (the source of the H^-: shown in Scheme I); this ion then alkylates benzene to give the diphenylbutane.



$$CH_3\underset{Ph}{CH}\overset{+}{C}HCH_3 + C_6H_6 \longrightarrow CH_3\underset{Ph}{CH}\text{-}\underset{Ph}{CH}CH_3 + H^+$$

9

In the case of higher secondary alkylbenzenes such as pentyl- and hexylbenzenes, there is a favored alternative fate for the carbocation intermediate analogous to **9**. For example, if hydride donation occurs from a secondary carbon in the 3 or 4 position of the side chain, intramolecular alkylation (cyclialkylation) may take precedence over the intermolecular alkylation which would produce diphenylalkanes. Consider the sequence of reactions in Scheme II. By the sequence of equations 1 + 2 + 3, two molecules of hexylbenzene may be converted into one molecule each of hexane, benzene, and 1-ethyl-3-methylindan, and by the sequence of equations 1 + 2 + 4 into hexane, benzene, and 1,4-dimethyltetralin. It is significant that these indan and tetralin derivatives are major components of the high-boiling aromatic reaction products. (Table VI, runs 26 and 33.)

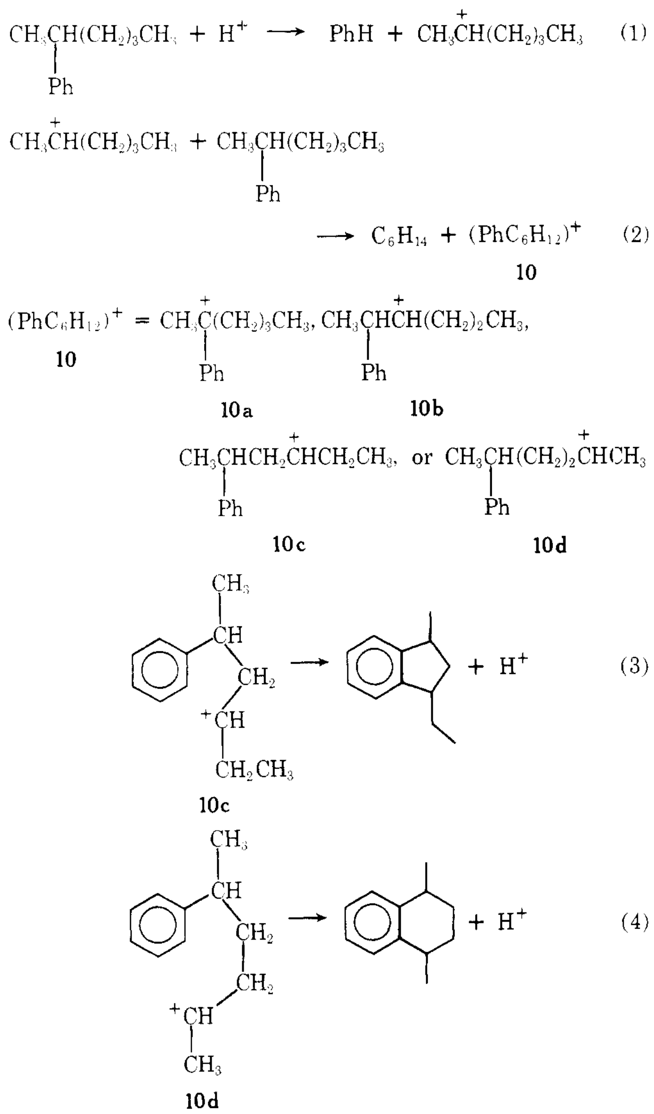
Another observation may be made about the results depicted in Table VI. This concerns the *absence* of branched chain hexylbenzene isomers such as 3-methyl-2-phenylpentane among the products. If the 2- and 3-methylpentanes came

Table VI. Rearrangement and Cyclialkylation Products from Secondary Hexylbenzenes

Run no.[a]	26	33	28	32
Starting material	2-PH[b]	3-PH[c]	2-PH[b]	3-PH[c]
Total products, %	29.3	27.6	57.4	46.0
3-Phenylhexane	3.0	2.3	4.0	5.8
2-Phenylhexane	6.0	4.2	1.0	2.3
2-Methyl-1-phenylpentane	0.9	1.1	0.6	0.3
1-Ethyl-3-methylindan	3.3	3.0	0.2	1.7
1,1,3-Trimethylindene	0.7	1.0		
1,3-Dimethyltetralin	1.6	1.6	2.0	2.3
1,4-Dimethyltetralin	5.0	3.4	2.4	4.5
1,3-Dimethylnaphthalene	2.5	5.5	2.0	1.5
1,4-Dimethylnaphthalene	1.3	1.8	0.4	0.2
1-Methyl-2-phenylcyclohexane			8.0	6.8
1-Methyl-4-phenylcyclohexane			34.0	17.4
Unidentified	5.0	3.7	2.8	3.2

[a] See Table III for experimental conditions. [b] 2-Phenylhexane. [c] 3-Phenylhexane.

Scheme II



$$\mathrm{CH_3\underset{Ph}{C}H(CH_2)_3CH_3 + H^+ \longrightarrow PhH + CH_3\overset{+}{C}H(CH_2)_3CH_3} \quad (1)$$

$$\mathrm{CH_3\overset{+}{C}H(CH_2)_3CH_3 + CH_3\underset{Ph}{C}H(CH_2)_3CH_3 \longrightarrow C_6H_{14} + \underset{\mathbf{10}}{(PhC_6H_{12})^+}} \quad (2)$$

$$\mathrm{\underset{\mathbf{10}}{(PhC_6H_{12})^+} = \underset{\mathbf{10a}}{CH_3\underset{Ph}{\overset{+}{C}}(CH_2)_3CH_3},\ \underset{\mathbf{10b}}{CH_3\underset{Ph}{C}H\overset{+}{C}H(CH_2)_2CH_3},\ \underset{\mathbf{10c}}{CH_3\underset{Ph}{C}HCH_2\overset{+}{C}HCH_2CH_3},\ or\ \underset{\mathbf{10d}}{CH_3\underset{Ph}{C}H(CH_2)_2\overset{+}{C}HCH_3}}$$

from dealkylation of branched chain hexylbenzenes produced by rearrangement prior to dealkylation, one would expect to find some of these branched chain hexylbenzenes among the reaction products. The only one detected was 2-methyl-2-phenylpentane, and it was a very minor component. These results are analogous to those from the pentylbenzenes, and they lend further support to the theory that the branched alkanes result from subsequent rearrangements of the straight chain secondary carbocations produced by initial cleavage from the aromatic ring. The wide difference in the proportions of normal and branched alkanes produced from *sec*-butylbenzene on the one hand and from secondary pentyl- and hexylbenzenes on the other hand is nicely rationalized in terms of protonated cyclopropane intermediates for the rearrangement of the straight chain secondary pentyl and hexyl carbocations to branched isomers, which then capture hydride ions to become branched alkanes. Since the corresponding protonated cyclopropane intermediate from *sec*-butyl cation cannot open to a branched isomer without acquiring primary carbocation character, much less isobutane than *n*-butane is formed.

Experimental Section

Materials. Anhydrous aluminum chloride (Mallinckrodt) was used as received. Aluminum bromide was prepared by the addition of bromine to aluminum powder and was distilled before use.[12] Fluoroantimonic acid (HF–SbF$_5$, 1:1) was used directly as received from Cationics, Inc. Benzene was commercial thiophene-free distilled and stored over sodium ribbon. *sec*-Butylbenzene was obtained from Aldrich Chemical Co. and was used as received. 2-Phenylpentane, 2-phenylhexane, and 3-methyl-2-phenylpentane were prepared by addition of the appropriate alkylmagnesium bromide to acetophenone, dehydration of the carbinol, and low-pressure hydrogenation of the alkene using palladium-on-charcoal catalyst in the presence of a small amount of perchloric acid.[13] 3-Phenylpentane, 3-phenylhexane, and 3-methyl-2-phenylbutane were synthesized by addition of phenylmagnesium bromide to the appropriate ketone, followed by dehydration and catalytic hydrogenation. 2- and 3-Bromohexane were made from the corresponding alcohols, triphenylphosphine, bromine, and dimethylformamide.[14] Authentic butanes, pentanes and hexanes were obtained from Phillips Petroleum Co.[15] All of the starting materials were checked for purity by infrared spectrophotometry and GLC before use.

Analytical Procedures. The hexanes produced by dealkylation were analyzed quantitatively and qualitatively by GLC using a 20 ft 10% SE-30 column at 30 °C. The pressure of the carrier gas, nitrogen, was 30 psi. The hexanes were identified by comparing their retention times with those of pure authentic compounds. In determining the mol % yield of hexanes, an exactly known weight of pure cyclohexane was added as an internal standard before each chromatographic analysis. Several other columns were used for analysis of the higher-boiling compounds, the best being a 6 ft 10% Ucon on 60–80 mesh Chromosorb P, with an oven temperature of 180 °C and a pressure of 20 psi of helium carrier gas. Mol % conversions to butanes and pentanes were based on the alkylbenzenes and were calculated from the volumes of gases collected. Most of the alkylbenzenes were identified by comparing their retention times with those of pure authentic compounds. Some were separated by preparative GLC and identified by NMR, IR, and mass spectrometry.

Dealkylation of Butyl- and Pentylbenzenes. The apparatus used in the experiments has been described before.[2] In a typical experiment, the alkylbenzene (0.10 mol) was added to aluminum chloride (0.033 mol), which had previously been activated by the addition of water (0.011 mol), and heated by an oil bath to 100 °C. After stirring the mixture for 3 h, the gases collected were analyzed by GLC. Mass spectrometry confirmed the analysis of some of the gases.

The liquid reaction mixtures were decomposed with ice water mixed with some acetone and worked up by ether extraction in the usual way. The solvent was distilled, and the products boiling between 80 and 220 °C were analyzed by GLC. The results of these experiments are given in Tables I and II.

Dealkylation of Hexylbenzenes. Two different procedures were used. **Procedure A.** The hexylbenzene and aluminum bromide were stirred and heated while a stream of nitrogen carried the volatile products through a trap containing 10% sodium hydroxide and then into a dry ice–acetone trap. In some experiments hydrogen bromide was passed into the hexylbenzene until the desired weight gain was obtained before aluminum bromide was added. The contents of the cold trap were taken up in ether and washed with water, 5% NaHCO$_3$ solution, and again with water. The ether solution was dried over anhydrous Na$_2$SO$_4$ and evaporated, and the residual organic material was weighed and analyzed by GLC. In one experiment (run 29) the reaction was carried out under a static nitrogen atmosphere using an ice water cooled reflux condenser protected by a drying tube. Thus, the dealkylation products were not removed from the rest of the reaction mixture, which was worked up in the usual way by careful addition of cold water. Further experimental details and results are given in Table III.

Procedure B. The reactions were carried out in a three-neck flask equipped with a magnetic stirrer, an addition funnel, and an ice water cooled condenser protected by a drying tube. The reactants were stirred at the temperatures and for the times specified in Table III, and then the reaction mixtures were quenched by the dropwise addition of ice-cold water. The organic layer was separated, the aqueous layer was extracted with two portions of ether which were combined with the organic layer, and the organic layer was then washed with 5% $NaHCO_3$ solution and two portions of water. The organic solution was dried over anhydrous Na_2SO_4 and weighed. A known weight of cyclohexane was added to serve as an internal standard, and a 5-mL aliquot of the mixture was taken for GLC analysis of the dealkylation products. The remainder of the reaction mixture was distilled, first at atmospheric pressure and then under reduced pressure. The fractions collected between 62 and 90 °C (2 mm) were analyzed by GLC, with the results presented in Table VI for four representative experiments.

The reactions in which HF–SbF_5 was used were carried out essetially according to procedure B. Details of experimental conditions and results are given in Table V.

Alkylation–Dealkylation with Bromohexanes as Starting Materials. These reactions were carried out as in procedure B except that the hexylbenzenes were produced in situ by reaction of 2- or 3-bromohexane with benzene under the conditions given in Table IV, with the results presented there. The rearrangement and cyclialkylation products were analyzed and found to be essentially the same as those formed from hexylbenzenes as starting materials (Table VI).

Registry No.—PhR (R = Me), 108-88-3; PhR (R = Et), 100-41-4; PhR (R = *n*-Pr), 103-65-1; PhR (R = *i*-Pr), 98-82-8; PhR (R = *sec*-Bu), 135-98-8; PhR (R - *i*-Bu), 538-93-2; PhR (R = *n*-Bu), 104-51-8; PhR (R = 2-Pe), 2719-52-0; PhR (R = 3-Pe), 1196-58-3; PhR (R = 2-methyl-1-butyl), 3968-85-2; 2-phenylhexane, 6031-02-3; 3-phenylhexane, 4468-42-2; 3-methyl-2-phenylpentane, 66418-14-2; 2-methylpentane, 107-83-5; 3-methylpentane, 96-14-0; *n*-hexane, 110-54-3; 2-bromohexane, 3377-86-4; 3-bromohexane, 3377-87-5; 2,2-dimethylbutane, 75-83-2; 2,3-dimethylbutane, 79-29-8; 2-methyl-1 phenylpentane, 39916-61-5; 1-ethyl-3-methylindan, 66418-15-3; 1,1,3-trimethylindene, 2177-45-9; 1,3-dimethyltetralin, 5195-37-9; 1,4-dimethyltetralin, 4175-54-6; 1,3-dimethylnaphthalene, 575-41-7; 1,4-dimethylnaphthalene, 571-58-4; 1-methyl-2-phenylcyclohexane, 17733-68-5; 1-methyl-4-phenylcyclohexane, 1603-60-7.

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(15) We thank Dr. Howard Bost for kindly providing these samples.

Kinetics of the Reactions of Weakly Basic Amines with Activated Aromatic Substrates. Reaction of Imidazole and Aniline with 1-Fluoro-2,4-dinitrobenzene

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Received November 11, 1977

The reactions named in the title were studied in water solution at different pH and buffer concentrations to search for the possibility of base catalysis in the addition step of nucleophilic aromatic substitution. The reaction of imidazole is independent of buffer and pH below pH 10.9 with a mean second-order rate constant of (1.09 ∓ 0.05) 10^{-3} M^{-1} s^{-1}. At higher pH the second-order rate constant increases linearly with hydroxide ion concentration. The rate acceleration was ascribed to the reaction of imidazole anion, the second-order rate constant of which is calculated as 0.195 M^{-1} s^{-1}. The reaction of aniline is independent of pH and buffer concentration below pH 10.56. At higher pH and higher ionic strength the reaction is slightly dependent on the phosphate trianion concentration, but this dependence changes with the compensating electrolyte used, and is attributed to a specific salt effect.

The study of reactions of amine nucleophiles has been of great importance in firmly establishing the multistep nature of the mechanism of aromatic nucleophilic substitution.[1]

The reactions of amines with compounds bearing poor leaving groups, such as methoxide ion, are base catalyzed with change in the rate-determining step at high base concentration,[2,3] whereas with substrates with good leaving groups such as chloride ion in protic solvents, base catalysis is not observed.[4]

The body of experimental results is consistent with the mechanism depicted in Scheme I, where $k_3{}^{\mathrm{B}}$ and $k_{-3}{}^{\mathrm{B}}$ are the rate constant for the proton transfer reactions, k_4 is the rate constant for the leaving group expulsion from **2**, and k_2 is the rate constant for the spontaneous or solvent-catalyzed elimination of HX from **1**.

Base catalysis is observed when the conversion of **1** to products is slower than the k_{-1} step. In such cases two different situations have been shown to occur.[5] In the first, $k_4 \gg k_{-3}{}^{\mathrm{B}}(\mathrm{BH})$ so that deprotonation of **1** is rate limiting in the base-catalyzed pathway. This situation is recognized by the