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## Alkylbenzenes. XII. Dealkylation and Fragmentation Reactions Induced by Aluminum Chloride-Water

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RECEIVED JUNE 8, 1963

The dealkylation and fragmentation reactions of ethyl-, propyl-, butyl-, and pentylbenzenes induced by heating with aluminum chloride-water have been studied. Products of these reactions were identified and analyzed by vapor phase chromatography and infrared spectrophotometry. A direct relationship was found between the primary, secondary, or tertiary structure of an alkyl side chain and its ease of cleavage by dealkylation. The order of susceptibility of tertiary > secondary > primary alkylbenzenes to dealkylation is responsible for the apparent small degree or lack of rearrangement of primary alkylbenzenes to secondary and tertiary isomers which have been observed previously. Identification of isobutane as the major initial gaseous dealkylation product from both *iso*- and *sec*-butylbenzene gave evidence of the rearrangement of both these isomers to *t*-butylbenzene, which was then rapidly dealkylated. Similar evidence was obtained of rearrangement of all of the other pentylbenzene isomers to *t*-pentylbenzene. Other molecules of alkylbenzenes serve as hydride donors in the dealkylation process; this leads to the formation of diphenylalkanes. *meso*-2,3-Diphenylbutane was isolated as a product from a reaction of *sec*-butylbenzene with aluminum chloride-water. Mechanisms of dealkylation are proposed which are reasonably related to the experimental results. Fragmentation reactions produced alkanes with fewer carbon atoms than the original alkyl side chains, and lower alkylbenzenes. The fragmentation patterns gave evidence for mechanisms involving cleavage of diphenylalkane intermediates to produce secondary or tertiary carbonium ions, and direct cleavage of some alkylbenzene molecules from which a tertiary alkyl carbonium ion will be produced.

## Introduction

In an earlier paper of this series,<sup>2</sup> the reactions which alkylbenzenes undergo when treated with Friedel-Crafts catalysts were classified as of five main types: (a) disproportionation (intermolecular alkyl transfers), (b) reorientation (intramolecular and/or intermolecular alkyl transfers), (c) rearrangement (internal, of side chains), (d) dealkylation (production of alkanes corresponding to alkyl side chains), and (e) fragmentation (production of alkanes smaller than alkyl side chains and smaller alkylbenzenes). There has been extensive investigation of the first three types in recent years,<sup>3</sup> but little attention has been given to the last two.

One of the earliest examples of dealkylation was the observation of a saturated gas evolved when *p*-cymene was heated with aluminum chloride, and the isolation of toluene from among the liquid products of this reaction.<sup>4</sup> The gas was later identified as propane, and various disproportionation products were found in addition to toluene, the liquid dealkylation product.<sup>5</sup> Similarly, isopropylbenzene was found to produce propane, but *n*-propylbenzene and *n*-butylbenzene under identical conditions were reported to give no alkanes.<sup>6</sup> The production of alkanes corresponding to the side chains of a series of alkylbenzenes, which were treated with aluminum chloride and a hydrogen donor such as cyclohexane, was demonstrated to take place with the ease of dealkylation in the order *t*-butyl > *sec*-butyl > isopropyl<sup>7</sup>; ethyl and methyl groups were not cleaved. The production of isobutane by treatment of *t*-butylbenzene with boron trifluoride-hydrogen fluoride was described<sup>8b</sup> and, recently, the dealkylation of *sec*-octyl- and dodecylbenzene by aluminum bromide.<sup>8b</sup>

Examples of fragmentation reactions of alkylbenzenes are even more scarce. Alkylation of benzene with *t*-

butyl alcohol and aluminum chloride at 80–95° was reported to give toluene, ethylbenzene, and isopropylbenzene, but no *t*-butylbenzene.<sup>8</sup> Ethylbenzene was identified among the products of alkylation of benzene with *n*-propyl ether with aluminum chloride catalyst,<sup>9</sup> and also in the mixture produced by heating isopropylbenzene with aluminum chloride.<sup>8g</sup>

We have now undertaken a systematic investigation of dealkylation and fragmentation reactions of alkylbenzenes, a study which is made feasible by modern instrumental methods, particularly vapor phase chromatography. This paper reports some of the results of such studies on ethyl-, propyl-, butyl-, and pentylbenzenes.

## Results and Discussion

Reactions between the alkylbenzenes and water-activated aluminum chloride were carried out in a closed system. The gaseous products were passed through a reflux condenser cooled by tap water, a sodium hydroxide solution to remove traces of hydrogen chloride, and collected over saturated salt solution. They were analyzed by vapor phase chromatography. The liquid reaction mixture (after the usual decomposition with water and extraction procedure) was distilled and analyzed by vapor phase chromatography and infrared spectrophotometry.

The fact that most of the alkylbenzenes studied undergo both dealkylation and fragmentation reactions at 100° is shown by the data in Tables I–IV.

The difficulty of studying the two types of reactions separately is illustrated by the behavior of *t*-butylbenzene. When it was heated with aluminum chloride-water at only 50° for 1 hr., 17 mole % of isobutane was evolved, and the liquid reaction mixture was found to contain toluene, ethylbenzene, isopropylbenzene, *sec*- and isobutylbenzene, and a small amount of recovered *t*-butylbenzene. Of course disproportionation occurs in all cases, having an effect on the recovery of mono-alkylbenzenes from the liquid reaction mixtures which is superimposed on the effects of dealkylation and fragmentation reactions. For example, note that only 30% of ethylbenzene was recovered, although very little dealkylation and practically no fragmentation of this hydrocarbon occurred. *n*-Butylbenzene gave very similar results. Examination of Tables I, III, and IV leads to the conclusion that there is a strong relationship between the primary, secondary, or tertiary struc-

(1) Robert A. Welch Foundation Post-doctoral Fellow.

(2) R. M. Roberts, G. A. Ropp, and O. K. Neville, *J. Am. Chem. Soc.*, **77**, 1764 (1955).(3) For leading references see (a) H. C. Brown and H. Jungk, *ibid.*, **77**, 5579 (1955); (b) D. A. McCauley and A. P. Lien, *ibid.*, **75**, 2411 (1953); (c) R. H. Allen, *ibid.*, **82**, 4856 (1960); (d) H. C. Brown and C. R. Smoot, *ibid.*, **78**, 2176 (1956); (e) D. V. Nightingale and J. M. Shackelford, *ibid.*, **78**, 1225 (1956); (f) L. Schmerling and J. P. West, *ibid.*, **76**, 1917 (1954); (g) C. D. Nenitzescu, I. Necsoiu, A. Glatz, and M. Zalman, *Chem. Ber.*, **92**, 10 (1959); (h) S. H. Sharman, *J. Am. Chem. Soc.*, **84**, 2945, 2951 (1962); (i) R. M. Roberts and Y. M. Han, *ibid.*, **85**, 1168 (1963).(4) R. Anschutz, *Ann.*, **235**, 177 (1886).(5) A. W. Schorger, *J. Am. Chem. Soc.*, **39**, 2671 (1917).(6) R. Heise and A. Töhl, *Ann.*, **270**, 155 (1892).(7) V. N. Ipatieff and H. Pines, *J. Am. Chem. Soc.*, **59**, 56 (1937).(8) J. F. Norris and B. M. Sturgis, *ibid.*, **61**, 1413 (1939).(9) S. Searles, *ibid.*, **76**, 2313 (1954).

TABLE I  
DEALKYLATION AND FRAGMENTATION PRODUCTS OF ETHYL-,  
PROPYL-, AND BUTYLBENZENES<sup>a</sup>

Start- ing ma- terial, R-C <sub>6</sub> H <sub>5</sub>	Liquid mixture, R-C <sub>6</sub> H <sub>5</sub> <sup>d</sup>								
	Gaseous products		Total, %	Me, %	Et, %	Pr, % <sup>f</sup>		Bu, % <sup>f</sup>	
	% <sup>b</sup>	Alkane <sup>c</sup>	% <sup>e</sup>	% <sup>f</sup>	% <sup>f</sup>	n-	i-	n-	sec/ <sup>g</sup>
Et	7	C <sub>2</sub> H <sub>6</sub>	30	tr	100				
<i>n</i> -Pr	7	C <sub>3</sub> H <sub>8</sub>	27	5	4	87	4		
<i>i</i> -Pr	18	C <sub>3</sub> H <sub>8</sub> <sup>h</sup>	17	2	22	Tr.	76		
<i>n</i> -Bu	4	<i>n</i> / <i>i</i> -C <sub>4</sub> H <sub>10</sub> <sup>i</sup>	37		0.5	0.5		97	2
<i>i</i> -Bu	15	<i>n</i> / <i>i</i> -C <sub>4</sub> H <sub>10</sub> <sup>i</sup>	20	18	10	2	5		65
<i>sec</i> -Bu	24	<i>n</i> / <i>i</i> -C <sub>4</sub> H <sub>10</sub> <sup>i</sup>	19	14	6	3	3		74
<i>t</i> -Bu	72	<i>i</i> -C <sub>4</sub> H <sub>10</sub>	3	25	56	5	12		2 <sup>k</sup>

<sup>a</sup> Reactions at 100° for 3 hr.; reactants: R-C<sub>6</sub>H<sub>5</sub>, 0.10 mole; AlCl<sub>3</sub>, 0.033 mole; H<sub>2</sub>O, 0.017 mole. <sup>b</sup> Mole % conversion to alkane based on alkylbenzene, calcd. from volume of gas collected. <sup>c</sup> Analyzed by v.p.c. <sup>d</sup> Boiling range 81-172°; benzene was produced in all expt. <sup>e</sup> Wt. % of original alkylbenzene; residue (b.p. >172°) was ca. 30 wt. %. <sup>f</sup> Percentage of each alkylbenzene in the liquid mixture. <sup>g</sup> Not resolved by v.p.c. <sup>h</sup> Traces of a hexane were found. <sup>i</sup> *n*/*i* = 36/64. <sup>j</sup> *n*/*i* = 70/30. <sup>k</sup> No *t*-butylbenzene was recovered.

TABLE II  
CHANGES IN DEALKYLATION AND REARRANGEMENT PRODUCTS  
FROM *sec*- AND ISOBUTYLBENZENE WITH TIME<sup>a</sup>

Time, min.	S.m. <sup>b</sup>	Butanes				Butylbenzenes		
		% <sup>c</sup>	Accumulated <sup>d</sup>	Current <sup>e</sup>		% <sup>f</sup>	<i>i</i> <sup>g</sup>	<i>sec</i> <sup>g</sup>
			<i>i</i> -	<i>n</i> -	<i>i</i> -	<i>n</i> -		
0.2 <sup>h</sup>	<i>s</i>	0.3 <sup>h</sup>	78	22	78	22		
	<i>i</i>	0.3 <sup>h</sup>	80	20	80	20		
1	<i>s</i>	2 <sup>h</sup>	39	61	30	70		
	<i>i</i>	2 <sup>h</sup>	66	34	63	37		
5	<i>s</i>	8	23	77	18	82	34	27
	<i>i</i>	7	30	70	20	80	30	75
10	<i>s</i>	13	19	81	12	88	26	58
	<i>i</i>	11	26	74	19	81	29	73
15	<i>s</i>	17	20	80	24	76	24	67
	<i>i</i>	14	26	74	26	74	28	69
30	<i>s</i>	21	22	78	33	67	22	68
	<i>i</i>	18	26	74	26	74	25	65
60	<i>s</i>	24	24	76	34	66	15	68
	<i>i</i>	19	26	74	27	73	21	64
120	<i>s</i>	26	25	75	34	66	14	68
	<i>i</i>	20	26	74	31	69	19	68
180	<i>s</i>	28	25	75	34	66	13	67
	<i>i</i>	21	27	73	34	66	13	68

<sup>a</sup> Temp., 100°; reactants: butylbenzene, 0.10 mole; AlCl<sub>3</sub>, 0.033 mole; H<sub>2</sub>O, 0.017 mole. <sup>b</sup> Starting material, *sec*- or isobutylbenzene. <sup>c</sup> Mole % conversion to butane based on butylbenzene, calcd. from volume of gas collected. <sup>d</sup> From direct v.p.c. analysis of gas collected during total time specified. <sup>e</sup> Calcd. ratio of isomers produced during most recent time interval. <sup>f</sup> Mole % recovered; b.p. 170-176°. <sup>g</sup> Infrared analysis. <sup>h</sup> Estimated; see Experimental section.

TABLE III  
GASEOUS DEALKYLATION AND FRAGMENTATION PRODUCTS FROM  
PENTYLBENZENES<sup>a</sup>

R-C <sub>6</sub> H <sub>5</sub>	Gaseous products					
	Total, % <sup>b</sup>	C <sub>2</sub> H <sub>6</sub> , % <sup>c</sup>	C <sub>3</sub> H <sub>8</sub> , % <sup>c</sup>		C <sub>4</sub> H <sub>10</sub> , % <sup>c</sup>	
			<i>n</i>	<i>i</i>	<i>n</i>	<i>i</i>
<i>n</i> -Pe	14			5	14	81
<i>i</i> -Pe	13	4	2	8	6	80
2-MeBu <sup>d</sup>	19	4	6	5	11	74
1-MeBu <sup>e</sup>	20			Tr.	4	96
1-EtPr <sup>f</sup>	27			1	13	86
neo-Pe <sup>g</sup>	18	1	1	15		83
1,2-diMePr <sup>h</sup>	40			27		73
<i>t</i> -Pe	56			28		72

<sup>a</sup> Reactions at 100° for 3 hr.; reactants: alkylbenzene, 0.10 mole; AlCl<sub>3</sub>, 0.033 mole; H<sub>2</sub>O, 0.011 mole. <sup>b</sup> Mole % conversion to alkane based on alkylbenzene, calcd. from volume of gas collected. <sup>c</sup> Percentage of each alkane in the gaseous mixture. <sup>d</sup> (2-Methylbutyl)-benzene. <sup>e</sup> (1-Methylbutyl)-benzene. <sup>f</sup> (1-Ethylpropyl)-benzene. <sup>g</sup> Neopentylbenzene. <sup>h</sup> (1,2-Dimethylpropyl)-benzene.

TABLE IV  
LIQUID DEALKYLATION AND FRAGMENTATION PRODUCTS FROM  
PENTYLBENZENES<sup>a</sup>

Starting material, R-C <sub>6</sub> H <sub>5</sub>	Liquid mixture, R-C <sub>6</sub> H <sub>5</sub> <sup>b</sup>								
	Total, % <sup>c</sup>	Me, % <sup>d</sup>	Et, % <sup>d</sup>	Pr, % <sup>d</sup>		Bu, % <sup>d</sup>		Pe, % <sup>d</sup>	
			<i>n</i>	<i>i</i>	<i>n</i>	<i>sec</i> / <i>i</i>	Orig.	Others	
<i>n</i> -Pe	35	5	5	4	4	5	70	7 <sup>e</sup>	
<i>i</i> -Pe	28	4	10		8	6	72		
2-MeBu <sup>f</sup>	28	1	4	3			92		
1-MeBu <sup>h</sup>	16	1	8	8		4	43	24 <sup>f</sup>	12 <sup>g</sup>
1-EtPr <sup>g</sup>	20	Tr.	6	5			18	50 <sup>h</sup>	20 <sup>f</sup>
neo-Pe <sup>i</sup>	41	6	2	2	2	2	85	1 <sup>i</sup>	
1,2-di-MePr <sup>k</sup>	13	1	4		8	4	5	78 <sup>j</sup>	
<i>t</i> -Pe	5	1	10	2	18	10	50 <sup>j</sup>	9 <sup>i</sup>	

<sup>a</sup> Conditions and reactants same as in Table III. <sup>b</sup> Boiling range, 100-200°. <sup>c</sup> Wt. % of original alkylbenzene; residue (b.p. >200°) was ca. 30 wt. %. <sup>d</sup> Percentage of each alkylbenzene in the liquid mixture. <sup>e</sup> Isopentylbenzene. <sup>f</sup> (2-Methylbutyl)-benzene. <sup>g</sup> (1-Ethylpropyl)-benzene. <sup>h</sup> (1-Methylbutyl)-benzene. <sup>i</sup> (1,2-Dimethylpropyl)-benzene. <sup>j</sup> Neopentylbenzene.

ture of the alkyl side chain and the extent of dealkylation and fragmentation reactions. This relationship would be even more obvious were it not for the rearrangements of some of the side chains; *i.e.*, there is little difference in the apparent degree of dealkylation and fragmentation of *sec*- and isobutylbenzene (as indicated by the second and fourth columns of Table I), but one must remember that rearrangement of the primary isobutylbenzene to *sec*-butylbenzene occurs under the conditions of the experiment. Although such rearrangements mask the relative susceptibilities of some of the primary and secondary alkylbenzenes to dealkylation and fragmentation, the extreme lability of the *t*-butyl- and pentylbenzenes is obvious from the data of Tables I, III, and IV. Ipatieff and Pines<sup>7</sup> observed this same order of reactivity (tertiary > secondary > primary) in dealkylation reactions in which a hydride donor was supplied (*e.g.*, cyclohexane). Our experiments show that addition of a cycloparaffin is not required to allow dealkylation of secondary and tertiary alkylbenzenes at significant rates. Apparently the alkyl side chains (and, perhaps, alkene dimers derived from the side chains<sup>10</sup>) can function as the hydride donors. There were few differences in results from experiments in which the pentylbenzenes were heated with aluminum chloride-water in the presence and absence of cyclohexane, except those which would be expected from the fact that the experiments with cyclohexane were carried out at lower temperatures. Both dealkylation and fragmentation were less extensive, but fragmentation did occur even under the milder conditions employed by Ipatieff and Pines, and the spectra of gaseous and liquid fragmentation products from the pentylbenzenes were similar to those obtained at 100° in the absence of cyclohexane.

It should be noted that the difference in the stability of *n*-propyl- and isopropylbenzene toward dealkylation and fragmentation reactions offers a reasonable explanation for the finding<sup>11,12</sup> that *apparently* only a small amount of rearrangement to isopropylbenzene accompanies the isotopic rearrangement of *n*-propyl- $\alpha$ (or  $\beta$ )-C<sup>14</sup>-benzene; undoubtedly more rearrangement to isopropylbenzene occurs than is observed. Similarly, it now seems quite likely that considerable rearrangement to *t*-butylbenzene accompanies the interconversion of iso- and *sec*-butylbenzenes, but none of the tertiary isomer is found owing

(10) We are indebted to one of the referees for calling this possibility to our attention.

(11) R. M. Roberts and S. G. Brandenberger, *Chem. Ind. (London)*, 227 (1955); *J. Am. Chem. Soc.*, **79**, 5484 (1957).

(12) R. M. Roberts and J. E. Douglass, *Chem. Ind. (London)*, 1557 (1958); *J. Org. Chem.*, **28**, 1225 (1963).

to its much greater susceptibility to dealkylation and fragmentation reactions (see also below).

Apparently, at 100° the rates of dealkylation and fragmentation reactions are of the same order of magnitude as rates of rearrangements of the side chains. If the rearrangements were much faster than the other reactions, the same proportions of dealkylation and fragmentation products would be produced from isomeric alkylbenzenes. This was not found. Although *similar* mixtures were produced from some of the butyl- and pentylbenzene isomers (*cf.* iso- and *sec*-butyl- in Table I), they were not identical and were sometimes quite different (*cf.* *n*-propyl- and isopropyl- in Table I).

The gas produced by both *sec*- and isobutylbenzene during a 3-hr. period at 100° was about a 2:1 mixture of *n*-butane and isobutane. In some of the experiments with shorter heating periods, the gas samples were found to contain different proportions of *n*-butane and isobutane. This led to a careful study of the changes in composition of the gaseous and liquid reaction products from iso- and *sec*-butylbenzene with time of heating with aluminum chloride-water at 100°. Results of these experiments are recorded in Table II. We were particularly interested in learning which alkane was produced initially from each alkylbenzene. Direct dealkylation would be expected to give *n*-butane from *sec*-butylbenzene, and isobutane from isobutylbenzene. Isobutane would also be produced, however, from *t*-butylbenzene, which is a possible rearrangement product of both *sec*- and isobutylbenzene.

It can be seen that the very first gas produced by dropping the hydrocarbon onto the hot catalyst was predominantly isobutane, regardless of whether the starting material was *sec*- or isobutylbenzene. Approximate rates of evolution of isobutane and *n*-butane from *sec*-butylbenzene at various times after addition of catalyst are presented in Table V; these were calculated from data of Table II.

TABLE V

RATES OF PRODUCTION OF ISOBUTANE AND *n*-BUTANE FROM *sec*-BUTYLBENZENE

Time, min.	0.1	0.6	3.0	7.5	12.5	23	45	90	150
Isobutane, ml./min.	35	14	8	3	5	2	1	0.3	0.2
<i>n</i> -Butane, ml./min.	10	31	35	23	15	7	2	0.6	0.4

Isobutane is evolved rapidly at first, but the rapid rate of production of this isomer is of short duration, and within a few minutes *n*-butane makes up the bulk of the gas being evolved. After about 20 min. the rate of production of *n*-butane has also diminished greatly, and slow evolution of both butanes continues in a ratio of about 2:1 in favor of *n*-butane. These results are not congruent with direct dealkylation of the butylbenzene isomers, but are explicable in the following terms. Both *sec*- and isobutylbenzene are rapidly isomerized to *t*-butylbenzene when first mixed with the hot catalyst, and the *t*-butylbenzene produced immediately undergoes dealkylation to isobutane and benzene. *sec*-Butylbenzene (either present originally or produced rapidly by isomerization) undergoes dealkylation to *n*-butane and benzene at a slower rate. Disproportionation of the butylbenzenes also occurs rapidly, and within 15-20 min. enough polyalkylbenzenes have been produced to deactivate the catalyst toward further rearrangement, dealkylation, and fragmentation reactions. (The ability of pentamethylbenzene to inhibit dealkylation was demonstrated by three experiments which are described in the Experimental section.)

The slow evolution of butanes which occurs after the first 15-20 min. probably represents the direct dealkylation of *sec*- and isobutylbenzene by the deactivated catalyst, in about a 2:1 ratio as would be expected.<sup>13</sup> Note that in accordance with this view, the rearrangement of *sec*- and isobutylbenzene was essentially complete after 15 min.; although presumably *sec*-butylbenzene is being dealkylated more rapidly than isobutylbenzene from this time on, the extent of dealkylation of both is too minor to affect the proportion of butylbenzene isomers significantly. Disproportionation and fragmentation reactions may also compensate so as to maintain the proportion of *sec*-/isobutylbenzene almost constant.

These data represent strong circumstantial evidence for the rearrangement of both *sec*- and isobutylbenzene to *t*-butylbenzene, and the momentary existence of the latter as a highly unstable intermediate before it is dealkylated. If the interconversions of *sec*- and isobutylbenzene follow mechanisms analogous to those proposed for the isotopic *n*-propylbenzene rearrangements, as we believe they do, the rearrangement to *t*-butyl- would be expected.<sup>14</sup> Probably it is only the extremely rapid rate of dealkylation of *t*-butylbenzene which precludes its detection among the liquid reaction products.

A similar conclusion can be drawn from the fact that the major alkane evolved from all of the pentylbenzenes was isopentane (Table III). Although *t*-pentylbenzene could not be detected among the liquid products from any of the pentylbenzene isomers, it was undoubtedly produced from all of them and was dealkylated rapidly.

An interesting side light was thrown on the mechanism of dealkylation (and fragmentation) by the isolation of *meso*-2,3-diphenylbutane as a minor product from the reaction of *sec*-butylbenzene with aluminum chloride-water. This material crystallized from one of the high-boiling distillates obtained from a liquid reaction mixture, after it had stood at room temperature many days. The pertinence of this finding is indicated in the discussion below.

**Mechanisms of Dealkylation Reactions.**—The probable course of dealkylation of alkylbenzenes by Lewis acid catalysts is outlined in Fig. 1, using *sec*-butylbenzene as an example. The production of a carbonium ion in eq. 2 is in line with the observed order of rate of dealkylation, *t*-alkyl > *sec*-alkyl > primary alkyl > methyl. Equation 3 represents the abstraction of a hydride ion by the carbonium ion to produce the alkane and a new phenylalkyl carbonium ion (IV), which may be in the form of IVa, b, or c. This ion rapidly alkylates either an alkylbenzene molecule (eq. 4) or a benzene molecule (eq. 5) [present owing to both the dealkylation (eq. 2) and to disproportionation]. Diphenylalkanes such as V and VI were expected among the high-boiling residues, and the isolation of *meso*-2,3-diphenylbutane was direct evidence of their presence. This specific compound could be produced directly by alkylation according to eq. 5 if IV is in the form of IVb or IVc, and, indirectly, if it is in the form of IVa, by subsequent rearrangement of the initially-formed 2,2-diphenylbutane.

(13) It is implicit in the explanation for the rapid initial evolution of isobutane from either *sec*- or isobutylbenzene, followed by slower evolution of a mixture of *n*-butane (mainly) and isobutane, that the rearrangements of the butylbenzenes require a more active catalyst than the dealkylations. Further investigation of the effect of deactivated catalysts on rearrangement and dealkylation processes is in progress.

(14) J. B. Douglass and R. M. Roberts, *Chem. Ind.* (London), 926 (1959); *J. Org. Chem.*, **28**, 1229 (1963). The mechanism of interconversion of *sec*- and isobutylbenzene and of rearrangement of each of these to *t*-butylbenzene can be extrapolated simply from the propylbenzene rearrangements of Fig. 1 on p. 1230 of the preceding reference, by substituting a methyl group for a hydrogen on the C<sup>14</sup>-labeled carbons in that figure.

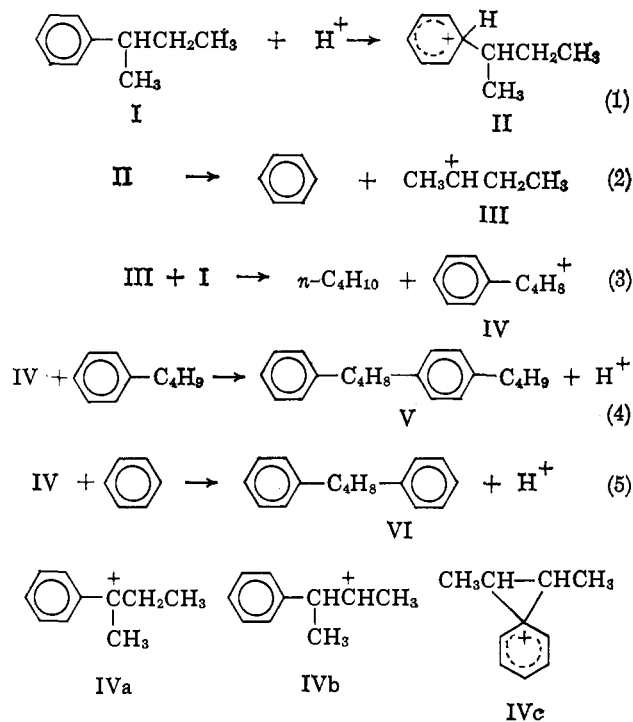


Figure 1.

**Mechanisms of Fragmentation Reactions.**—A clue to the mechanisms of fragmentation reactions is given by the observation that no methane or ethane was ever found among the gaseous products from any of the alkylbenzenes higher than ethylbenzene. (Tests showed that they would have been detected by the vapor phase chromatographic analysis.) Assuming some kind of carbonium ion mechanism, an obvious explanation for the absence of methane and ethane lies in the fact that secondary and tertiary carbonium ions may be intermediates for propane and butane and higher alkanes, but not for methane and ethane. However, fragmentation products are found which obviously involve loss of one- and two-carbon units from the original alkylbenzene; *i.e.*, propylbenzene yields toluene and ethylbenzene (Table I). Hence, a mechanism of fragmentation must be sought which can accommodate the preferential formation of three-carbon and higher alkanes as well as loss of one- and two-carbon units from the side chains. This is not as difficult as might at first appear, and it is interesting that the accidental isolation of *meso*-2,3-diphenylbutane lends support to a mechanism of fragmentation as well as to the mechanism of dealkylation described above.

Most of the carbon-carbon bond cleavages in the side chains probably occur in diphenylalkane molecules such as *meso*-2,3-diphenylbutane, since these produce more stable carbonium ion intermediates than would be obtained by cleavages in simple alkylbenzenes. For example, the formation of ethylbenzene from one of the butylbenzenes may involve the sequences shown in Fig. 2 to produce *meso*-2,3-diphenylbutane, which then undergoes cleavage as shown.

Evidence supporting this suggestion was afforded by the treatment of *meso*-2,3-diphenylbutane with aluminum chloride-water at 70°. The liquid products in the 100–200° boiling range were found to be mainly *sec*-isobutylbenzene and ethylbenzene, with minor amounts of isopropylbenzene, *n*-propylbenzene, and toluene.

The production of toluene and ethylbenzene from *n*-propylbenzene can be explained in terms of an analogous mechanism in which 1,2-diphenylpropane is an intermediate. We shall not attempt to outline detailed

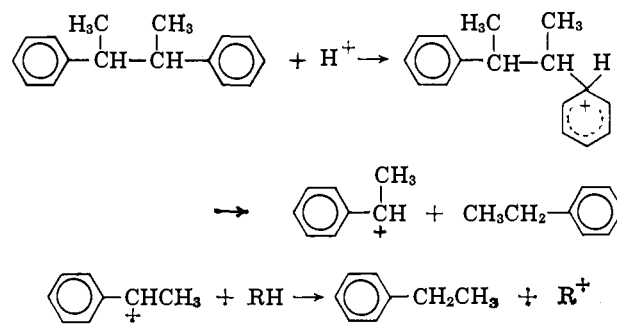
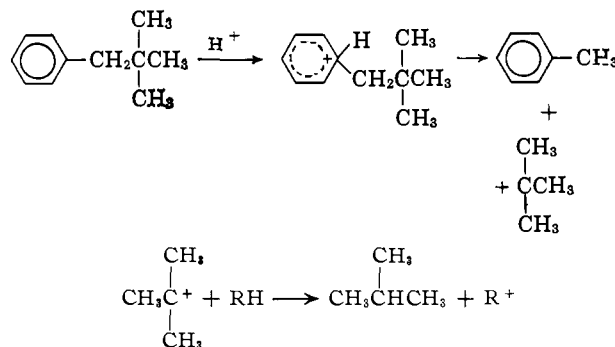


Figure 2.

mechanisms for the formation of all of the observed fragmentation products; many of them can be reasonably explained by similar sequences of alkylation, dealkylation, rearrangement, and cleavage. It is possible that direct cleavage in an alkylbenzene side chain may occur when a tertiary alkyl carbonium ion will result. The predominance of isobutane as a fragmentation product from neopentylbenzene and the two isomeric pentylbenzenes which rearrange to neopentylbenzene<sup>15</sup> (*cf.* Tables III and IV) may be indicative of direct cleavage to toluene and *t*-butyl carbonium ion<sup>15</sup>



Further work designed to afford better understanding of these complex reactions is in progress.

### Experimental

**Materials.**—The alkylbenzenes were either best quality commercial chemicals or were synthesized by unequivocal conventional methods. They were checked for purity by vapor phase chromatography and infrared analysis before use. Aluminum chloride was B and A, anhydrous sublimed reagent, used as received.

**Reactions of Ethyl-, Propyl-, and Butylbenzenes.**—The reactions were carried out in a flask equipped with a Teflon-covered magnetic stirrer, a pressure-equalized addition funnel, and a reflux condenser which led to a trap containing sodium hydroxide solution, followed by a safety trap. The gases were collected over saturated salt solution, and their volumes were read after equalizing the pressure. The whole apparatus was flushed with helium before use; this eliminated an air peak from the vapor phase chromatographic (v.p.c.) analyses. The reaction flask was heated by an electrically heated oil bath which maintained the temperature within about  $\pm 2^\circ$ .

In a typical experiment, the alkylbenzene (0.10 mole) was added to aluminum chloride (0.033 mole) which had been previously activated by the addition of water (0.017 mole) and heated by an oil bath to 100°. After stirring the mixture for 3 hr., the gases collected were analyzed by v.p.c. (see below). Mass spectrometry confirmed the analysis of some of the gases. The liquid reaction mixtures were decomposed with ice-water and worked up by ether extraction in the usual way. After the removal of ether and benzene, the mixture of alkylbenzenes boiling between the b.p. of benzene and slightly above the b.p. of the original alkylbenzene was analyzed by v.p.c. and infrared spectrophotometry (see below). The results of these experiments are given in Table I.

(15) It is interesting to note in this connection that addition of hydrogen chloride to 1-phenyl-2-methyl-1-propene gave 1-phenyl-2-methyl-2-chloropropane rather than 1-phenyl-1-chloropropane, which appears to indicate that the tertiary alkyl ion  $\text{C}_6\text{H}_5\text{CH}_2\text{C}^+(\text{CH}_3)_2$  is more stable than the secondary benzyl ion  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}^+(\text{CH}_3)_2$  [R. H. Hall, R. G. Pyke, and G. F. Wright, *J. Am. Chem. Soc.*, **74**, 1597 (1952)].

Two experiments in which *t*-butylbenzene was heated at 50° (other conditions as above) for 1 hr and 3 hr., respectively, gave the following results: (1 hr.) 17 mole % conversion to isobutane, 10 wt. % recovery of alkylbenzenes, b.p. 100–200°, consisting of toluene (16%), ethylbenzene (47%), isopropylbenzene (34%), *sec*-isobutylbenzene (5%), and *t*-butylbenzene (3%); (3 hr.) 35 mole % conversion to isobutane, 7 wt. % recovery of alkylbenzenes, b.p. 100–200°, consisting of toluene (17%), ethylbenzene (54%), isopropylbenzene (21%), *n*-propylbenzene (2%), and *sec*-isobutylbenzene (6%).

**Studies on the Changes in Dealkylation and Rearrangement Products from *sec*- and Isobutylbenzene with Time.**—These experiments were carried out as described above (at 100°), except that the reactions were carried out for shorter periods of time and, at the end of each reaction, the gaseous products were swept into the receiver with a stream of helium so as to collect the total alkanes produced in a given time. The gaseous mixture was analyzed directly by v.p.c. The liquid reaction mixture was worked up in the usual way and the distillation fraction containing recovered *sec*- and isobutylbenzenes, b.p. 170–176°, was analyzed by infrared spectrophotometry. The results are presented in Table II.

The data given in the first lines of Table II (on the gases evolved in 1 min. and less after hydrocarbon was added to catalyst) were obtained in a special way. A syringe was inserted through a rubber bulb covering one neck of the reaction flask and samples were withdrawn about 10 sec. and 1 min. after the addition of the hydrocarbon to the catalyst. The volumes of gas produced at these times were estimated by extrapolation from the volumes at 5 and 10 min.

Tests were made in which pure *n*-butane and isobutane were passed into mixtures of aluminum chloride–water and benzene under the conditions of the dealkylation experiments. No isomerization of the butanes occurred.

**Tests on Deactivation of the Catalyst toward Dealkylation.**

**A.—*sec*-Butylbenzene** (0.10 mole) was heated with aluminum chloride (0.033 mole) and water (0.017 mole) at 100° as described above. After 3 hr. the evolution of butane and isobutane, which had amounted to 29% of the theoretical amount, had virtually stopped. The apparatus was flushed with helium, and aluminum chloride (0.033 mole) and water (0.017 mole) were added. A brisk evolution of gas occurred immediately; it was mainly isobutane and *n*-butane, in the same proportions at different times as described in Table II, but about 4% of propane was present in the gas evolved during the first 10 min. after the second batch of catalyst was added. The volume of gas produced after 1 hr. corresponded to an additional 24% of dealkylation, and the evolution of gas had practically stopped again (an amount equivalent to only 0.5% occurred in an additional hour).

**B.**—Another reaction was run as in A. Five minutes after the reaction was initiated, ca. 9% dealkylation had occurred and the evolution of gas was steady. At this stage, 14.8 g. (0.10 mole) of melted pentamethylbenzene was added. The gas evolution stopped abruptly and no more occurred in the next 2 hr.

**C.**—A mixture of aluminum chloride (0.033 mole), water (0.017 mole), and pentamethylbenzene (0.10 mole) was stirred at 100° for 2 min. and then *sec*-butylbenzene (0.10 mole) was

added. There was no evolution of gas either immediately or within the next 2 hr.

**Isolation of *meso*-2,3-Diphenylbutane.**—Reaction of 0.2 mole of *sec*-butylbenzene with aluminum chloride and water at 100° for 3 hr. was carried out and the liquid reaction mixture was decomposed with water as before. The organic material was distilled, 29 wt. % being obtained in the range 100–200° with a composition similar to that reported in Table I. The pot residue was distilled under reduced pressure, giving fractions a, b.p. 80–110° (3 mm.), 2.5 g.; b, b.p. 110–130° (3 mm.), 1.7 g.; c, b.p. 130–200° (3 mm.), 0.5 g.; residue, ca. 3 g. Fraction b crystallized partially upon prolonged standing. Recrystallized from ethanol, 0.42 g. of crystals, m.p. 124–126°, was obtained, identified as *meso*-2,3-diphenylbutane by mixture m.p. with authentic material and by identity of its infrared spectrum with that of authentic material.

**Reaction of *meso*-2,3-Diphenylbutane with Aluminum Chloride.**

—A mixture of 10 g. (0.05 mole) of *meso*-2,3-diphenylbutane, 2.7 g. (0.02 mole) of aluminum chloride, and 1 drop of water was heated with stirring at 70° for 1 hr. The solid hydrocarbon formed a red, homogeneous solution within a few minutes after being mixed with aluminum chloride and warmed to 70°. The reaction mixture was poured into ice–water and extracted with two 50-ml. portions of ether. The ether extracts were washed with water, dried over calcium chloride, and distilled through an 80-cm. Nichrome spiral column. The distillate, b.p. 100–200°, 2.1 g., was shown by v.p.c. to consist of *sec*-isobutylbenzene (50%), ethylbenzene (45%), isopropylbenzene (3%), and *n*-propylbenzene (2%).

**Reactions of Pentylbenzenes. A. With Aluminum Chloride and Water.**

—These experiments were carried out as those with ethyl-, propyl-, and butylbenzenes, except that a mixture of the hydrocarbon (0.10 mole) and water (0.011 mole) was added to the aluminum chloride (0.033 mole) in a flask heated by an oil bath at 100°. Data on gaseous products are given in Table III and data on liquid products are given in Table IV.

**B. With Aluminum Chloride, Water, and Cyclohexane.**

—These experiments were carried out as described above, except that a molar equivalent of cyclohexane was added, and the temperature was kept at 57–60°. Some butanes were identified in the gases evolved, and some lower alkylbenzenes were found in each liquid reaction mixture, in about the same proportions as in the absence of cyclohexane at 100°.

**Analysis.**—Vapor phase chromatographic analysis was made with a Beckman GC2A instrument, fitted with a 6-ft. column packed with silicone oil on firebrick. The carrier gas was helium at 30 p.s.i.; temperatures compatible with the boiling points of the samples were used.

Infrared analyses were made with a Beckman IR-5A instrument, with sodium chloride prism and cells. Quantitative analyses of mixtures of *sec*- and isobutylbenzene were carried out in isooctane solutions as described previously.<sup>16</sup>

**Acknowledgment.**—We wish to thank the National Science Foundation and the Robert A. Welch Foundation for grants which supported this research.

(16) R. M. Roberts, Y. W. Han, C. H. Schmid, and D. A. Davis, *J. Am. Chem. Soc.*, **81**, 640 (1959).

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## The Aminolysis of Thioacyl and Selenoacyl Analogs<sup>1,2</sup>

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RECEIVED JULY 8, 1963

The relative rates of the reaction of N,S-dibenzoylselenocysteamine and of N,S-dibenzoylcysteamine with *n*-butylamine were investigated; the former compound was found to undergo aminolysis much more rapidly than the latter. This difference in reactivity was found to be due to a relatively favorable entropy of activation in the case of the selenoacyl compound.

Sulfur compounds as diverse as thioesters, sulfonium compounds, and anhydrides of sulfuric and phosphoric acids play an important part in biological energy and group transfer reactions. While numerous comparative studies of the reactions of oxygen and sulfur analogs have been carried out, the interpretation of differences

(1) A preliminary account of part of this material appeared in *J. Am. Chem. Soc.*, **83**, 3342 (1961). Portions of this work were presented before the I.U.P.A.C. Congress, London, July, 1963.

(2) We are indebted to the National Science Foundation and to the United States Public Health Service for their support of this work.

in reaction rates and mechanism have been complicated by differences in the atomic radii of oxygen and of sulfur.<sup>3</sup> This factor is of particular importance in obscuring the meaning of observed differences in the entropies of activation of oxygen and sulfur analogs. However, steric considerations play a less important part when the reactivities of sulfur and selenium analogs are compared, the atomic radii of sulfur and selenium being rather similar<sup>3</sup>

(3) I. Pauling in "The Nature of the Chemical Bond," 3rd. Ed., Cornell University Press, Ithaca, N. Y., 1960, pp. 246, 260.