

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

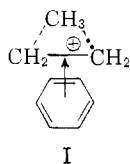
Alkylbenzenes. V. Interconversion of *sec*-Butylbenzene and Isobutylbenzene<sup>1</sup>

BY ROYSTON M. ROBERTS, YURI W. HAN, CALVIN H. SCHMID AND DONALD A. DAVIS

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The butylbenzene fraction recovered after treatment of either *sec*-butylbenzene or isobutylbenzene with wet aluminum chloride at 100° has been found to contain these two isomeric hydrocarbons in an equilibrium ratio of 1/2, with only negligible amounts of *t*-butylbenzene present. The dibutylbenzenes produced by disproportionation also contained the same distribution of isomeric side chains. These results can be correlated with the isotopic rearrangement of *n*-propyl- $\beta$ -C<sup>14</sup>-benzene by assuming the same type of methyl-bridged  $\pi$ -complex intermediate and are thus considered to support the previously proposed mechanism.

In previous papers we have described the behavior of C<sup>14</sup>-labeled ethylbenzene, *n*-propylbenzene and *n*-butylbenzene upon treatment with aluminum chloride.<sup>2,3</sup> The observed extensive rearrangement of *n*-propyl- $\beta$ -C<sup>14</sup>-benzene to *n*-propyl- $\alpha$ -C<sup>14</sup>-benzene and the lack, or much smaller degree, of rearrangement of (1) *n*-propyl- $\beta$ -C<sup>14</sup>-benzene to *n*-propyl- $\gamma$ -C<sup>14</sup>-benzene or isopropylbenzene, (2) ethyl- $\beta$ -C<sup>14</sup>-benzene to ethyl- $\alpha$ -C<sup>14</sup>-benzene, and (3) *n*-butyl- $\alpha$ -C<sup>14</sup>-benzene to *n*-butyl- $\beta$ -C<sup>14</sup>-benzene or *sec*-butylbenzene are difficult to explain in terms of a carbonium ion mechanism. In an attempt to correlate the observed facts, a mechanism was proposed for the isotopic rearrangement of *n*-propylbenzene which involves as an intermediate a methyl-bridged  $\pi$ -complex, I, and the failure to find appreciable rearrangements of the other types listed above was attributed to the lesser ability of hydrogen or methylene to function as a bridge in a similar intermediate. Since this



postulated mechanism was admittedly based to a considerable extent on negative evidence, it was desirable immediately to seek positive evidence in the form of other extensive rearrangements which might also involve methyl-bridged  $\pi$ -complex intermediates.

Among other alkylbenzenes having the requisite structure for rearrangement *via* such an intermediate are *sec*-butylbenzene and isobutylbenzene, which represent  $\alpha$ - and  $\beta$ -methyl substituted derivatives of *n*-propylbenzene. If the mechanism proposed for the isotopic rearrangement of *n*-propylbenzene were followed by isobutylbenzene and *sec*-butylbenzene, they should be interconverted, as shown in Fig. 1. The detection of such a rearrangement can be made, of course, without recourse to isotopic labeling. Although the boiling points of isobutylbenzene and *sec*-butylbenzene differ by only half a degree, their infrared and mass spectra are sufficiently distinctive to allow both qualitative

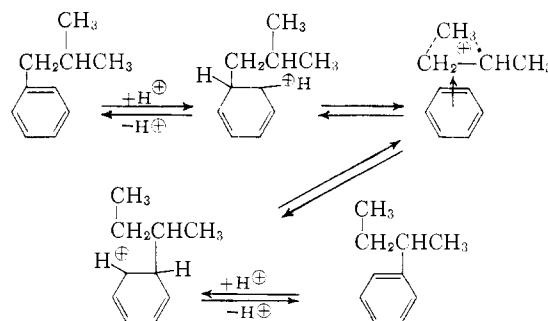


Fig. 1.

and quantitative analysis of mixtures. This is true also of the other two isomeric butylbenzenes, *n*-butylbenzene and *t*-butylbenzene.<sup>4</sup>

The results of a series of experiments with isobutylbenzene are summarized in Table I. Preliminary tests in which isobutylbenzene was heated with aluminum chloride showed that it underwent disproportionation to form a mixture containing benzene, butylbenzenes, dibutylbenzenes and higher alkylated benzenes, as expected. This mixture was separated by fractional distillation. The nature of the recovered butylbenzene fraction was the major interest of this investigation. This was determined by means of infrared analysis as described in the experiment section. The infrared spectra of dibutylbenzene fractions from two disproportionations (expts. 5 and 12, Table I) were determined; strong absorption peaks at 12.7 and 14.2  $\mu$  indicated that they were mainly *m*-dibutylbenzenes.<sup>5</sup> However, since analysis of the dibutylbenzene fractions would be complicated by the presence of both *m*- and *p*-isomers, no further steps in such an analysis were taken. From the experience with *n*-propyl- $\beta$ -C<sup>14</sup>-benzene, it was expected that the isomeric distribution of the side chains would be the same in the butylbenzenes and dibutylbenzenes. This was confirmed by "transalkylating" benzene with dibutylbenzenes and examining the butylbenzenes produced (expts. 4 and 17, Table I).

When isobutylbenzene was stirred with aluminum chloride at room temperature for 6.5 hr., disproportionation occurred, but the butylbenzene fraction was found to be pure isobutylbenzene (expt. 1). However, the butylbenzene fraction recovered after heating isobutylbenzene at 100° for 0.5 hr. was a mixture of isobutylbenzene (26%) and *sec*-

(1) (a) Paper IV, R. M. Roberts and S. G. Panayides, *J. Org. Chem.*, **23**, 1080 (1958); (b) part of this work was reported at the 133rd Meeting of the American Chemical Society, San Francisco, Calif., April 18, 1958.

(2) R. M. Roberts, G. A. Ropp and O. K. Neville, *THIS JOURNAL*, **77**, 1764 (1955).

(3) R. M. Roberts and S. G. Brandenberger, *ibid.*, **79**, 5484 (1957).

(4) The infrared spectra of all four butylbenzenes are given in the reports of A. P. I. Project No. 44.

(5) Cf. G. F. Hennion, A. J. Driesch and P. L. Dee, *J. Org. Chem.*, **17**, 1102 (1952).

TABLE I  
 ISOMERIZATION OF *sec*- AND ISOBUTYL BENZENE BY ALUMINUM CHLORIDE

Expt.	Starting materials	Catalyst <sup>a</sup>	Temp., °C.	Time, hr.	Butylbenzene products, % <sup>b</sup>	
					<i>s</i> -BuPh	<i>i</i> -BuPh
1	<i>i</i> -BuPh	AlCl <sub>3</sub> <sup>c</sup>	25-30	6.5	0	100 <sup>d</sup>
2		AlCl <sub>3</sub> <sup>c</sup>	100	0.5	26	74
3		AlCl <sub>3</sub> <sup>c</sup>	100	6.5	30	70
4	Bu <sub>2</sub> C <sub>6</sub> H <sub>4</sub> <sup>e</sup> + C <sub>6</sub> H <sub>6</sub>	AlCl <sub>3</sub> <sup>c</sup>	100	4.0	33	67
5	<i>i</i> -BuPh	AlCl <sub>3</sub> <sup>c</sup>	100	1.0	32	68
6		AlCl <sub>3</sub> + H <sub>2</sub> O <sup>f</sup>	100	0.25	27	78
7		AlCl <sub>3</sub> + H <sub>2</sub> O <sup>f</sup>	100	1.0	34	68
8	<i>s</i> -BuPh	AlCl <sub>3</sub> + H <sub>2</sub> O <sup>g</sup>	25-30	24.0	100	0
9		AlCl <sub>3</sub> + H <sub>2</sub> O <sup>g</sup>	50	6.0	90	14
10		H <sub>2</sub> SO <sub>4</sub> <sup>h</sup>	100	1.0	100	0
11		AlCl <sub>3</sub> <sup>i</sup>	100	1.0	65	30
12		AlCl <sub>3</sub> <sup>c</sup>	100	1.0	49	51
13		AlCl <sub>3</sub> + H <sub>2</sub> O <sup>g</sup>	100	1.0	34	67
14		AlCl <sub>3</sub> + H <sub>2</sub> O <sup>f</sup>	100	1.0	33	66
15		AlCl <sub>3</sub> + H <sub>2</sub> O <sup>f</sup>	100	1.0	33	66
16		AlCl <sub>3</sub> <sup>c</sup>	100	6.0	29	66
17	Bu <sub>2</sub> C <sub>6</sub> H <sub>4</sub> <sup>j</sup> + C <sub>6</sub> H <sub>6</sub>	AlCl <sub>3</sub> <sup>c</sup>	100	1.0	34	66

<sup>a</sup> AlCl<sub>3</sub>/BuPh mole ratio was in all expts. 0.32. <sup>b</sup> From infrared analysis in isoöctane solution. <sup>c</sup> Anhydrous aluminum chloride exposed to air several minutes. <sup>d</sup> The values in the first four expts. were determined by comparison of infrared spectrograms of pure butylbenzenes (no solvent). <sup>e</sup> Dibutylbenzene fraction from expt. 3. <sup>f</sup> Equimolar amounts. <sup>g</sup> One drop (24 mg.) of water added to 10.85 g. of AlCl<sub>3</sub>. <sup>h</sup> H<sub>2</sub>SO<sub>4</sub>/BuPh mole ratio was 0.32. <sup>i</sup> Anhydrous AlCl<sub>3</sub> was opened and mixed with BuPh in a dry-box. <sup>j</sup> Dibutylbenzene fraction from expt. 15.

butylbenzene (74%) (expt. 2); there was no evidence of the presence of any *tert*-butylbenzene or *n*-butylbenzene. Increasing the time of heating to 6.5 hr. increased the proportion of *sec*-butylbenzene only slightly (expt. 3). The butylbenzene fraction obtained by transalkylation of the dibutylbenzene fraction from the same expt. consisted of almost the same proportion of isomers.

When *sec*-butylbenzene was heated with aluminum chloride at 100° for 6 hr. (expt. 16), the butylbenzene fraction recovered was found to be a mixture of *sec*-butylbenzene and isobutylbenzene, in approximately the same proportions as when isobutylbenzene was the starting material (expt. 3). This ratio of isobutylbenzene to *sec*-butylbenzene of 2 to 1 appears to be the equilibrium value, and hence must represent the thermodynamic stability of the two hydrocarbons under the conditions of the experiments.

Neitzescu<sup>6</sup> has emphasized the importance of water in promoting aluminum chloride-catalyzed rearrangements of aliphatic and alicyclic hydrocarbons. Having had difficulty in reproducing some of the experiments on rearrangement of *n*-propyl- $\beta$ -C<sup>14</sup>-benzene, we suspected that the presence or absence of water might have an effect on the activity of the aluminum chloride. In all the experiments mentioned so far, anhydrous aluminum chloride was allowed to stand in air a few minutes before added to the hydrocarbons. Experiments 11-14 represent a series in which results from *sec*-butylbenzene and catalyst exposed in this way to adventitious moisture (expt. 12) were compared with those from catalyst carefully excluded from moisture (expt. 11), from catalyst to which a known small amount of water was added (expt. 13), and from catalyst to which an equimolar amount of water was added (expt. 14). Although there was some rearrangement in expt. 11, it was appreciably less

than in expt. 12, and that in expt. 12 was less than the equilibrium value found in both expts. 13 and 14. Experiments 6 and 7 show that the isomerization of isobutylbenzene by wet aluminum chloride is complete in less than an hour at 100°. It thus appears that water plays an important role in the catalysis, and it may be that the actual catalyst is the strong acid H<sup>+</sup> AlCl<sub>3</sub>OH<sup>-</sup>, as suggested by Neitzescu.<sup>6</sup> In an early experiment (not included in Table I), hydrogen chloride was added to the aluminum chloride-butylbenzene mixture. The composition of the recovered butylbenzene fraction was the same as in the absence of hydrogen chloride; *e.g.*, isobutylbenzene/*sec*-butylbenzene = 2/1.

Rearrangement of *sec*-butylbenzene was inappreciable at room temperature in 24 hr. (expt. 8). At 50° for 6 hr., a small amount of rearrangement occurred (expt. 9). Of course, disproportionation was extensive in both experiments. Experiments 14 and 15 were carried out under identical conditions; the compositions of the butylbenzene fractions were identical, the equilibrium value. The butylbenzene fraction obtained by transalkylation of the dibutylbenzene fraction from expt. 15 had the same composition.

Experiment 10 represents a test in which sulfuric acid was substituted for aluminum chloride. No disproportionation occurred and the infrared spectrum of the recovered *sec*-butylbenzene showed it to be unchanged.

The butylbenzene fractions from expts. 5, 13 and 16 were subjected to mass spectroscopic analysis.<sup>7</sup> The results are given in Table II. The percentages of isobutylbenzene were in fairly close agreement with the infrared analyses. It is particularly noteworthy that *no t*-butylbenzene was found in the samples from expts. 5 and 13, and only 0.6% in

(6) C. D. Neitzescu, M. Avram and E. Sliam, *Bull. soc. chim. France*, 1266 (1955).

(7) We wish to thank Dr. William A. Bailey, Jr., Shell Oil Co., Houston, Texas, for this analysis.

TABLE II  
MASS SPECTROSCOPIC ANALYSIS OF BUTYLBENZENE FRACTIONS

Butylbenzene fraction, expt.	5	13	16
Composition, volume %			
C <sub>8</sub> -Alkylbenzene	0.6	1.5 <sup>a</sup>	3.0 <sup>a</sup>
<i>i</i> -Butylbenzene	69.6	66.9	64.9
<i>s</i> -Butylbenzene	29.8	30.4	29.1
<i>t</i> -Butylbenzene	..	..	0.6
C <sub>11</sub> -Alkylbenzenes	..	0.5	1.7
C <sub>12</sub> -Alkylbenzenes	..	.3	0.4
C <sub>13</sub> -Alkylbenzenes	..	.1	.1
C <sub>14</sub> -Alkylbenzenes	..	.3	.2

<sup>a</sup> For purposes of calculation, this was assumed to be mesitylene.

the sample from expt. 16.<sup>8</sup> The boiling range of the butylbenzene fractions of Table II was 170–172.5°, and one sample which was analyzed in the mass spectroscope (but was not included in Tables I and II because its infrared analysis was not complete) had a boiling range of 166–177°, yet it contained no *t*-butylbenzene.

It is somewhat surprising that the interconversion of these two butylbenzenes by aluminum chloride has not been observed before. Perhaps this is true partly because it was so unexpected, particularly in the direction *sec*-butylbenzene → isobutylbenzene, since this involves the conversion of a secondary into a primary alkylbenzene. In the only experiment in which they heated *sec*-butylbenzene with aluminum chloride (at 100° for 3 hr.), Eliel, Wilken and Fang reported recovering a butylbenzene fraction which had an infrared spectrum "almost identical to that of 2-phenylbutane but showing slight contamination which manifested itself especially in a strong band at 13.6 μ."<sup>9</sup> The contaminant was undoubtedly isobutylbenzene; the 13.5 μ (or 13.6 μ) band is the strongest in its spectrum which differs from those of *sec*-butylbenzene.

McCaulay and Lien described the disproportionation of *sec*-butylbenzene and di-*sec*-butylbenzene with hydrogen fluoride and boron trifluoride and found no isomerization of the butyl groups,<sup>10</sup> but this is not surprising since they operated at room temperature.

The only other examples, to our knowledge, in which *sec*-butylbenzenes or isobutylbenzenes have been heated with aluminum chloride and a careful scrutiny made of the reaction products are the isomerizations of 1,3-dimethyl-4-butylbenzenes described by Nightingale and Shackelford.<sup>11</sup> They reported that the isobutyl and *sec*-butyl groups migrated from the 4- to the 5-position without rearrangement. Although Dr. Nightingale has advised us<sup>12</sup> that, because of the complexity of the

products, it would be difficult to rule out some rearrangement of butyl groups, we would not consider lack of rearrangement in these molecules necessarily to be in conflict with our results. It is clear that the migration of an alkyl group on an aromatic ring into a position *meta* to other alkyl groups is extremely rapid, often taking place without accompanying disproportionation.<sup>13</sup> Undoubtedly this occurred rapidly in the experiments of Nightingale and Shackelford, and the 1,3,5-trialkylbenzenes produced, being strongly basic, may have complexed with the aluminum chloride to such an extent that the catalyst would not be active enough to cause isomerization of the *iso*-butyl and *sec*-butyl groups.

However, it may be appropriate to express a word of caution about accepting without scrutiny the structure of an alkylbenzene having *sec*-butyl groups which has been heated in the presence of aluminum chloride. Although it may not contain any *t*-butyl groups, the possibility of the presence of isobutyl groups should not now be overlooked.

We should like to re-emphasize the fact that the interconversion of isobutylbenzene and *sec*-butylbenzene by water-activated aluminum chloride without the concurrent formation of appreciable amounts of *t*-butylbenzene<sup>14</sup> is, in terms of previously accepted mechanisms, at least as inexplicable as the isotopic rearrangement of *n*-propylbenzene, and of considerably greater practical importance. The postulate of a new mechanism of rearrangement involving a methyl-bridged π-complex intermediate which was made to explain the isotopic *n*-propylbenzene rearrangement is considerably supported by the results from isobutylbenzene and *sec*-butylbenzene. We are continuing this investigation by seeking to bring to light other rearrangements of alkylbenzenes which appear to involve a methyl-bridged π-complex intermediate. As evidence of the reality of this intermediate accumulates, we hope to find an answer to the question of why a methyl group should provide a much more facile avenue for rearrangement than a hydrogen or methylene group.

## Experimental

**Materials.**—*sec*-Butylbenzene was Phillips Pure Grade (99 mole % minimum). It was distilled through an 80-cm. Nichrome spiral column, b.p. 171–172.5°. Its infrared spectrum was identical with that recorded as Serial No. 508 by A. P. I. Project No. 44.

Isobutylbenzene was synthesized from isobutyric acid (Eastman Kodak Co.) and thiophene-free benzene by conversion to isobutyrophenone in the usual way,<sup>15</sup> followed by Wolff-Kishner reduction.<sup>16</sup> The product was distilled through the 80-cm. column, b.p. 170–172.5°. Its infrared spectrum was identical with that recorded as Serial No. 412 by A.P.I. Project No. 44.

(13) (a) D. A. McCaulay and A. P. Lien, *THIS JOURNAL*, **74**, 6246 (1952); (b) H. C. Brown and H. Jungk, *ibid.*, **77**, 5579 (1955).

(14) The recent work of L. G. Cannell and R. W. Taft, Jr. [*THIS JOURNAL*, **78**, 5812 (1956)] illustrates the multiplicity of products to be expected from a carbonium ion process. Although carbonium ions such as would be formed by abstraction of a hydride ion from isobutylbenzene or *sec*-butylbenzene would be different from a simple isobutylcarbonium ion, it is hard to believe that interconversion *via* rearrangements of such ions could occur without the formation of some *tert*-butylbenzene.

(15) E. Berliner and F. Berliner, *ibid.*, **72**, 222 (1950).

(16) Huang-Minlon, *ibid.*, **68**, 2487 (1946).

(8) We had previously ascertained that as little as 5% of *t*-butylbenzene could be detected in synthetic mixtures with isobutylbenzene and *sec*-butylbenzene by infrared analysis, and the spectra of the reaction products gave no indication of even this amount. Mass spectroscopic analysis for *t*-butylbenzene is still more precise, however.

(9) E. L. Eliel, P. H. Wilken and F. T. Fang, *J. Org. Chem.*, **22**, 231 (1957).

(10) D. A. McCaulay and A. P. Lien, *THIS JOURNAL*, **75**, 2411 (1953).

(11) D. V. Nightingale and J. M. Shackelford, *ibid.*, **76**, 5767 (1954).

(12) D. V. Nightingale, private communication.

*t*-Butylbenzene was synthesized from *t*-butyl chloride and benzene in the usual way. Its infrared spectrum was checked with Serial No. 414, A.P.I. Project No. 44.

Isooctane (2,2,4-trimethylpentane) was Merck Reagent, suitable for spectrophotometric use.

Aluminum chloride was B. and A., Anhydrous Sublimed, Reagent.

Infrared analysis was made by means of a Baird Associates model No. 4-55 double-beam recording spectrophotometer, equipped with sodium chloride optics. The absorption peaks which were most useful were: isobutylbenzene, 8.5, 9.0, 9.1, 13.5  $\mu$ ; *sec*-butylbenzene, 10.0, 10.4, 13.1  $\mu$ . Analyses of the products of expts. 1-4 (Table I) were made on pure liquid samples in cells of about 0.02-mm. thickness. The other analyses were made on isooctane solutions containing 5% by weight of butylbenzenes, using a sample cell of 0.188-mm. thickness and a reference cell (filled with solvent) of 0.187-mm. thickness. The spectra of 5% isooctane solutions of pure *sec*-butylbenzene, isobutylbenzene and 20-80%, 40-60%, 60-40% and 80-20% mixtures were recorded using the same cells. These spectra were the basis of construction of a plot of optical density at 13.1 and 13.5  $\mu$  vs. percentage composition of mixtures of the two butylbenzenes. This plot is available on microfilm.<sup>17</sup> The analyses

(17) Deposited as Document number 5709 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress,

of the butylbenzene fractions from expts. 5-17 were made by comparison of the absorption of their solutions at 13.1 and 13.5  $\mu$  with this plot. Complete spectrograms (2-16  $\mu$ ) of the pure butylbenzene fractions were also made in most of the expts. for qualitative comparisons.

**Treatment of *sec*-Butylbenzene and Isobutylbenzene with Aluminum Chloride.**—The conditions of temperature, catalyst and time of treatment are given in Table I. In all expts., the hydrocarbon and aluminum chloride were stirred continuously in a round-bottomed flask equipped with a reflux condenser protected by a calcium chloride tube. In most experiments, the amount of butylbenzene treated was 34 g. At the conclusion of the catalyst treatment, cold water was added cautiously and the hydrocarbons were isolated as described previously. The benzene, butylbenzene, and, in some experiments, the dibutylbenzene fractions were separated by distillation through a 50-cm. glass helices-packed column (expts. 1-4) or an 80-cm. Nichrome spiral column (expts. 5-17). The butylbenzene fractions were collected over a boiling range of 165-175° in expts. 1-4, and 170-172.5° in expts. 5-17.

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AUSTIN 12, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

## The Direction of Elimination in the Pyrolysis of Acetates<sup>1</sup>

BY DONALD H. FROEMSDORF, CAROL H. COLLINS, GEORGE S. HAMMOND AND CHARLES H. DEPUY<sup>2</sup>

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The pyrolysis of a number of aliphatic and alicyclic acetates has been re-examined. The products were analyzed by gas chromatography. The most striking result is the randomness in the reaction. Superimposed upon the nearly statistical results are small electronic and steric effects which often oppose each other. The pyrolysis of 1-alkylcyclohexyl acetates gives predominantly endocyclic olefins. It is suggested that, in contrast to the pyrolysis of amine oxides, the transition state in acetate pyrolysis does not require exact eclipsing of the hydrogen and the acetoxy group.

The pyrolysis of acetates is a useful procedure for the preparation of many unsaturated compounds. Applied to primary acetates, which can give only a single elimination product, the reaction is often the method of choice for the preparation of pure olefins. Although secondary and tertiary acetates might be expected to give mixtures of products, it has been recently reported<sup>3,4</sup> that such esters show remarkable specificity in pyrolysis. That olefin which would be predicted by the Hoffman rule,<sup>5</sup> *i.e.*, the least substituted ethylene, was believed to be formed nearly exclusively. We have recently reported that the pyrolysis of 1,3-diaryl-2-propyl acetates gives predominantly the more stable olefins<sup>6</sup> (*i.e.*, Saytzeff rule<sup>5</sup>). Consideration of the results led us to re-examine the pyrolysis of aliphatic acetates. The study was facilitated by the use of gas chromatography as an analytical tool. The results obtained are not in agreement with the previously published generalization.<sup>3,4</sup> In one instance we have been able to show that results, based upon infrared analyses

previously obtained in this Laboratory, are in error.<sup>7</sup> In fact, with a single possible exception, all pyrolyses gave mixtures.

### Results

A series of aliphatic acetates was first studied for comparison with earlier results. The reactions were carried out by dropping pure, liquid esters into the top of a vertical Vycor or Pyrex tube which was packed with Pyrex helices or beads. Pyrolysis tubes were heated externally. A slow stream of nitrogen was used to sweep the gases through the tube and products were collected in a Dry Ice trap. The conversion was determined by titration of the acetic acid in aliquots from the product mixtures. Low-boiling, olefinic products were usually separated from acetic acid and unreacted ester by distillation and the distillate was analyzed by gas chromatography. High boiling reaction mixtures, and occasionally low boiling products, were sampled directly and the samples of unrectified pyrolysate were chromatographed. The product mixture from the pyrolysis of 1-methylcyclohexyl acetate was also analyzed by nuclear magnetic resonance absorption spectroscopy.<sup>8</sup> Examination of the infrared spectrum of the same mixture showed that agreement with the other two analytical

(1) This research was supported by grants from the Petroleum Research Fund administered by the American Chemical Society and from the Office of Ordnance Research. Grateful acknowledgment is hereby made to the donors of said funds.

(2) To whom inquiries and requests for reprints should be sent.

(3) W. J. Bailey and C. King, *THIS JOURNAL*, **77**, 75 (1953).

(4) W. J. Bailey, J. J. Hewitt and C. King, *ibid.*, **77**, 357 (1955).

(5) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 427.

(6) G. H. DePuy and R. E. Leary, *THIS JOURNAL*, **79**, 3705 (1957).

(7) T. D. Nevitt and G. S. Hammond, *ibid.*, **76**, 4124 (1954).

(8) We are indebted to Dr. Keith McCallum, Rohm and Haas Co. Redstone Arsenal Research Division, for the nuclear magnetic resonance analysis.