It is consistent with these observations to suggest that in 100% sulfuric acid V exists partly as the lactol carbonium ion (Vc) and partly as the acylium ion (Vd). Consistent with this view is the lessened absorption at 3975 Å. compared with the other methoxy benzoylbenzoic acids. One further attempt to obtain insight into this question was unsuccessful. The n.m.r. spectrum of V in 100% sulfuric acid revealed the methoxyl signal as a sharp singlet. The fluorine n.m.r. spectrum of 2-(4′-fluorobenzoyl)benzoic acid also showed the fluorine signal as a singlet in 100% H_2SO_4. Hence, there is no n.m.r. evidence for two species, but rapidly equilibrating species may be present.

ρ–σ Correlations.—The general pattern of the ρ–σ type of correlations is clear in Table I. Plotting the equilibrium constants against σ^+ values for the substituents gives a reasonably good single straight line for substituents in both rings. The value for 4-nitro-2-benzoylbenzoic acid (VII) lies distinctly off the line. It is to be noted that nitro compounds often give difficulty in such determinations of equilibria by spectral means. Omitting VII, the least-squares correlation gives $\rho = 1.83$, $\sigma = 0.977$.

Experimental

The preparation and characterization of the compounds used in this study have been described previously. The methods for determining the ionization ratios have been described previously.[17]

---

[17] D. S. Noyce and M. J. Jorgenson, *J. Am. Chem. Soc.*, **84**, 4312 (1962)

Synthesis and Isomerization of 2,6-Dimethyl-*n*-butylbenzene

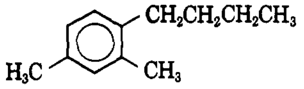
F. E. Condon[1] and Andreas A. Zavitsas

Department of Chemistry, The City College of the City University of New York, New York, New York

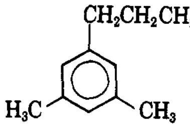
Received November 3, 1964

A new hydrocarbon, 2,6-dimethyl-*n*-butylbenzene, has been synthesized and its isomerization–disproportionation by aluminum chloride at 100° has been studied and compared with that of 2,4-dimethyl-*n*-butylbenzene. Both isomerisates contain at least 17 components and are much more complex than indicated by previous work. Migration and intermolecular transfer of methyl groups as well as the *n*-butyl group were noted. The *n*-butyl group is not rearranged. A time study of the isomerization of 2,6-dimethyl-*n*-butylbenzene showed the early formation of xylenes as potential intermediates for the formation of isomers by butyl group transfer, suggested that 2,4-dimethyl-*n*-butylbenzene is an intermediate in the transformation of 2,6- to 3,5-dimethyl-*n*-butylbenzene, and indicated that the disappearance of 2,6-dimethyl-*n*-butylbenzene is kinetically second order in the parent hydrocarbon.

It is now well established that the aluminum chloride catalyzed isomerization of 2,4-dimethyl-*n*-butylbenzene (I) takes place without rearrangement of the *n*-butyl group and gives 3,5-dimethyl-*n*-butylbenzene (II) as the major product.[2] An earlier report[3] that 3,5-dimethyl-*t*-butylbenzene (III) was the major product—an identification based on physical properties and the preparation of derivatives—seems now to have been incorrect. In related work, the aluminum chloride catalyzed disproportionation of *n*-butylbenzene has been shown to take place without rearrangement of the *n*-butyl group and to give mainly 1,3-di-*n*-butylbenzene, and the aluminum chloride catalyzed alkylation of benzene with 1,3-di-*n*-butylbenzene gives solely *n*-butylbenzene.[4]



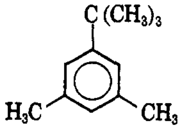
I



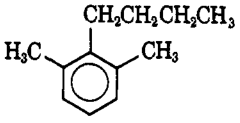
II

Much controversy has centered around the question whether the isomerization of alkylbenzenes takes place intramolecularly or intermolecularly, and at least five distinct mechanisms have been proposed. Some of these will be referred to later in the discussion.

In order to extend knowledge in this area and to try to resolve some of the controversy regarding the mechanism of alkylbenzene isomerization, we have synthesized 2,6-dimethyl-*n*-butylbenzene (IV) and made a time study of its isomerization by aluminum chloride at 100°. At the same time, we have repeated the synthesis and isomerization of I, in order to be able to compare the behavior of I and IV toward aluminum chloride.



III



IV

Synthesis.—The synthesis of IV made use of *t*-butyl as a removable blocking group[5] as shown in the accompanying sequence (Scheme I). Compounds IV–VIII are new. An attempt to reduce V to VIII by the Clemmensen method failed, perhaps because of steric hindrance.[6]

Comparative Isomerizations of 2,4- and 2,6-Dimethyl-*n*-butylbenzene.—The isomerization of 2,6-dimethyl-*n*-butylbenzene was carried out as described previously for 2,4-dimethyl-*n*-butylbenzene[2,3] by heating it 3.5 hr. on a steam bath with 22% of its weight of anhydrous aluminum chloride. Isomerization of 2,4-dimethyl-*n*-butylbenzene was conducted similarly except that only 17% by weight of aluminum chloride was used. Each reaction mixture was washed, dried, and distilled under reduced pressure. Each yielded a volatile fraction distilling to 132° at 17 mm. and com-

---

[1] To whom communications should be sent.

[2] D. V. Nightingale and J. M. Shackelford, *J. Am. Chem. Soc.*, **76**, 5767 (1954).

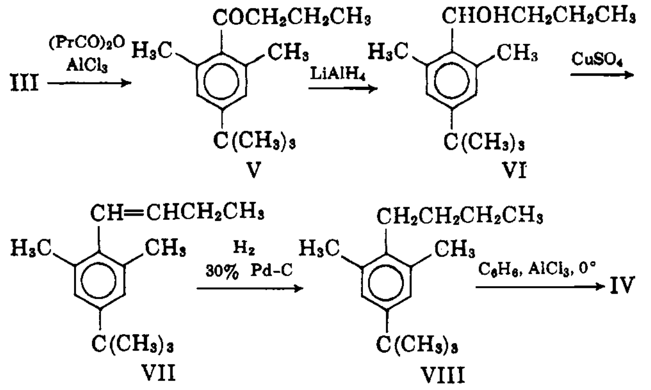
[3] D. Nightingale and L. I. Smith, *ibid.*, **61**, 101 (1939).

[4] R. E. Kinney and L. A. Hamilton, *ibid.*, **76**, 786 (1954).

[5] M. J. Schlatter, *ibid.*, **76**, 4952 (1954).

[6] *Cf.* F. C. Whitmore and C. T. Lester, *ibid.*, **64**, 1251 (1942).

SCHEME I



prising 71–72% by weight of the material recovered, and a higher boiling residue comprising 28–29%.

Each volatile isomerisate was subjected to gas–liquid chromatographic analysis, and an infrared spectrum of each was obtained. The g.l.c. analysis revealed at least 17 components in the isomerisate from 2,6-dimethyl-*n*-butylbenzene, as shown in Table I. Most of the same components appeared to be present in the isomerisate from 2,4-dimethyl-*n*-butylbenzene, and in similra proportions, except that the percentage conversion appeared to be smaller in the latter case. The reaction mixture is much more complex than indicated by the earlier report.[2] Migration and intermolecular transfer of methyl groups has occurred, as well as of the *n*-butyl group.

TABLE I

COMPOSITIONS OF ISOMERISATES FROM 2,4- AND 2,6-DIMETHYL-*n*-BUTYLBENZENE[a]

Component	Retention time, min.	%[b] from 2,6-Me₂-*n*-BuC₆H₃	%[b] from 2,4-Me₂-*n*-BuC₆H₃	Identity
1	0.95	0.1	0.3	Benzene
2	1.50	0.4		Toluene
3	2.36	9.9	5.1	*m*- and *p*-Xylene
4	2.84	2.0	0.7	*o*-Xylene
5	3.70	2.8	1.6	
6	4.30	9.0	5.2	1,2,4-Trimethylbenzene[c]
7	5.30	1.7	0.7	(Two-component peak)
8	*d*	2.8[e]	8.7	*x*-Tetramethylbenzene[e]
9	7.95	13.0[e]		*x*-*n*-Butyltoluene[e]
10	8.80	1.4	3.1	
11	11.5	28.5	40.3	3,5-Dimethyl-*n*-butylbenzene
12	12.6	16.8	34.3	2,5-Dimethyl-*n*-butylbenzene
13	13.0			2,4-Dimethyl-*n*-butylbenzene
14	13.8	6.4		2,6-Dimethyl-*n*-butylbenzene
15	15.4	0.4	Discontinued	
16	21.1	3.7		
17	23	1.1		

[a] The fraction distilling to 132° at 17 mm. and comprising 71–72% of recovered material. [b] Observed g.l.c. peak areas reduced to 100% basis. [c] Identified by n.m.r. spectroscopy. [d] A shoulder on the peak for component 9. [e] Relative amounts and identities of components 8 and 9 are based on the n.m.r. spectrum of 8–9 peaks which were incompletely resolved by g.l.c.

Of particular interest in the gas–liquid chromatographic record was a major peak (component 9, Table I) having the same retention time as 3,5-dimethyl-*t*-butylbenzene. This peak was preceded by a shoulder indicative of incomplete separation from another component (8). For further analysis, two 30-μl. samples of the volatile isomerisate from 2,6-dimethyl-*n*-butylbenzene were put through an Aerograph A-700 instrument with a 6-m. silicone column operated at 182°, and a sample of material corresponding to components 8 and 9 was collected. Samples were also collected of component 6 (Table I) and the major isomerization product, component 11. These samples were examined by n.m.r. spectroscopy, and an infrared spectrum of component 11 was obtained.

By comparison with spectra of authentic samples, component 6 was shown to be 1,2,4-trimethylbenzene, and component 11 was shown to be 3,5-dimethyl-*n*-butylbenzene.

The n.m.r. spectrum of component 8–9 was consistent with what would be expected for a mixture that was 18% a tetramethylbenzene and 82% a *n*-butyltoluene. Approximate τ values, assignments, relative peak areas observed, and peak areas calculated for such a mixture follow: 3.04, aromatic ring H, 3.54, 3.64; 7.5, benzylic methylene H, 1.72, 1.64; 7.8, benzylic methyl H, 4.59, 4.59; 8.5, aliphatic methylene H, 3.26, 3.28; 9.1, aliphatic methyl H, 2.48, 2.46.

Benzene, toluene, the xylenes, and 2,5-dimethyl-*n*-butylbenzene were identified by their retention times. When mixtures of isomerisate and authentic samples of these hydrocarbons were chromatographed, enhancement of corresponding peaks in the chromatographic record was noted.

The presence of 2,4-dimethyl-*n*-butylbenzene in the isomerisate from 2,6-dimethyl-*n*-butylbenzene was inferred from some complexity of the chromatographic record in the region where it would have been eluted. We could not be sure, however, of the presence of 2,6-dimethyl-*n*-butylbenzene in the isomerisate from 2,4-dimethyl-*n*-butylbenzene.

The only two remaining positional isomers, namely, 2,3- and 3,4-dimethyl-*n*-butylbenzene, may have been present, in view of the presence of *o*-xylene. If so, however, their chromatographic peaks were obscured by those of the other isomers mentioned.

Time Study of 2,6-Dimethyl-*n*-butylbenzene Isomerization.—In Table II are presented results of a time study of the isomerization of 2,6-dimethyl-*n*-butylbenzene, in which about 4% of tetrachloroethylene was present as an internal gas–liquid chromatographic standard. Samples of the entire reaction mixture were analyzed, rather than a volatile distillate as in the experiments of Table I.

Perhaps the most noteworthy feature of the data in Table II is the apparent buildup of xylenes to a nearly steady-state concentration. Isomers appear to be formed, then, by an intermolecular mechanism by way of disproportionation products. Recent evidence indicates that such disproportionation products are formed by way of 1,1-diarylalkanes[7,8] rather than by way of an SN2-type displacement of one arene by another on benzylic carbon, as had been proposed earlier,[9] but our data are consistent with either of these intermolecular mechanisms.

Either mechanism involves, in essence, an electrophilic attack on an aromatic nucleus. Such attack

---

(7) A. Streitwieser, Jr., and L. Reif, *J. Am. Chem. Soc.*, **82**, 5003 (1960); **86**, 1988 (1964).

(8) R. M. Roberts, A. A. Khalaf, and R. N. Greene, *ibid.*, **86**, 2846 (1964).

(9) D. A. McCaulay and A. P. Lien, *ibid.*, **75**, 2411 (1953).

TABLE II

TIME STUDY OF 2,6-DIMETHYL-*n*-BUTYLBENZENE ISOMERIZATION[a]

Peak	Component	Time, min. 18	41	71	108
		% composition[b]			
1	Benzene	0.9	0.8	0.8	0.6
2	Toluene	0.4	0.5	0.6	0.6
3	*m*- and *p*-xylene	13.0	14.0	12.4	11.4
4	*o*-Xylene	1.9	2.3	1.8	1.7
5		0.2	0.4	0.8	1.2
6	1,2,4-Trimethylbenzene	2.3	4.4	5.0	6.0
7	(Two-component peak)	0.6	1.1	1.1	1.2
8	*x*-Tetramethylbenzene	3.5	7.8	(8.8)[c]	9.8
9	*x*-*n*-Butyltoluene				
10					
11	3,5-Dimethyl-*n*-butylbenzene	7.6	15.8	18.5	22.2
12	2,5-Dimethyl-*n*-butylbenzene	(26.4)[c,d]	(19.4)[c,d]	(19.3)[c,d]	(20.3)[c,d]
13	2,4-Dimethyl-*n*-butylbenzene				
14	2,6-Dimethyl-*n*-butylbenzene	44.9	26.6	17.9	14.4
	Total	101.7	93.1	87.0	89.4

[a] About 4% of tetrachloroethylene was present as an internal gas–liquid chromatographic standard. [b] Peak area percentage of original 2,6-dimethyl-*n*-butylbenzene. [c] Numbers in parentheses are uncertain. [d] Total area under incompletely separated peaks 11–14, less areas estimated for peaks 11 and 14.

would take place on *m*-xylene preferentially in the 4-position, which is *ortho* to one methyl and *para* to the other, rather than in the 5-position, which is *meta* to both. Our time study data in Table II suggest that this happens and that 2,4-dimethyl-*n*-butylbenzene is an intermediate to 3,5-dimethyl-*n*-butylbenzene.

One other observation worth noting is the apparent second-order kinetics for the disappearance of 2,6-dimethyl-*n*-butylbenzene. From the data in Table II, second-order rate constants calculated by the equation, $k_2 = (1/c - 1)/t$, are 0.0682, 0.0673, 0.0646, and 0.0550 min.$^{-1}$, where c is the mole fraction of 2,6-dimethyl-*n*-butylbenzene remaining at time, t. First-order rate constants, calculated by the equation, $k_1 = (2.303 \log 1/c)/t$, are not nearly so constant: 0.0445, 0.0324, 0.0243, and 0.0185 min.$^{-1}$.

The second-order kinetics are consistent with a bimolecular mechanism for transfer of the *n*-butyl group but are somewhat surprising in view of the presumption that *m*-xylene and other components of the reaction mixture may act as acceptors of the *n*-butyl group from 2,6-dimethyl-*n*-butylbenzene.

One of many conceivable mechanistic pathways—one making use of 1,1-diarylalkane intermediates proposed by Streitwieser and Reif[7]—is shown in Figure 1. A kinetic interpretation is not justified, however, because of the many alternative pathways conceivable.

Experimental

2,6-Dimethyl-4-*t*-butylphenyl Propyl Ketone (V).—To a mixture of 320 ml. of carbon disulfide, 259 g. (1.60 mole) of 3,5-dimethyl-*t*-butylbenzene,[3] and 237 g. (1.50 mole) of *n*-butyric anhydride was added, with stirring and cooling in the course of 1.5 hr., 454 g. (3.40 moles) of anhydrous aluminum chloride. The reaction mixture was poured onto ice, separated, washed with water and sodium bicarbonate solution, dried with anhydrous magnesium sulfate, and distilled under reduced pressure. Material boiling at 120–139° (2 mm.) was collected and weighed 297 g. (85% yield). A fraction boiling at 128–130° (2 mm.) was taken for analysis.

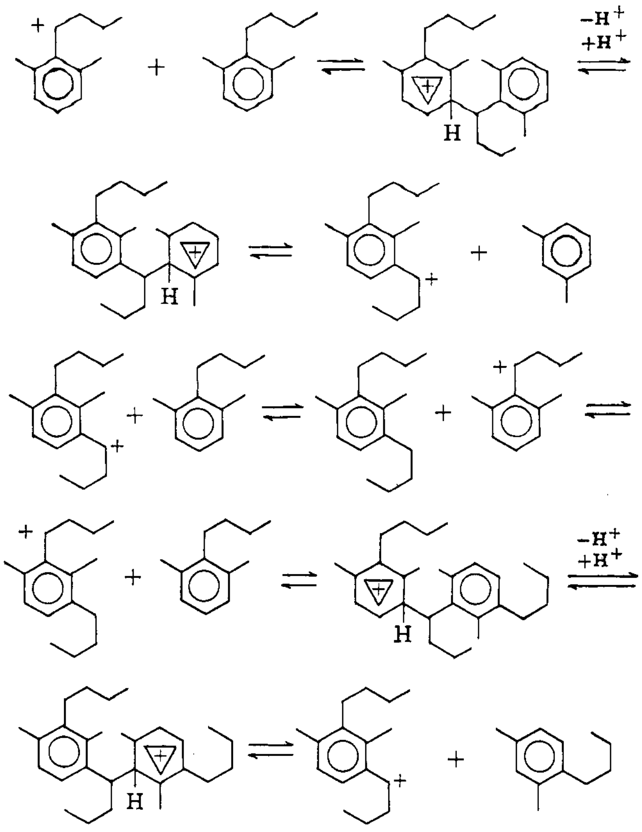


Figure 1.—One of many conceivable mechanistic pathways for 2,6-dimethyl-*n*-butylbenzene isomerization, involving 1,1-diarylalkane intermediates.

Anal.[10] Calcd. for $C_{16}H_{24}O$: C, 82.68; H, 10.43. Found: C, 83.06; H, 10.01.

2,6-Dimethyl-4-*t*-butylphenylpropylcarbinol (VI).—A mixture of 500 ml. of dry ethyl ether and 15.0 g. (0.40 mole) of lithium aluminum hydride was refluxed with stirring for 1 hr. To the resulting suspension a mixture of 296 g. (1.27 mole) of 2,6-dimethyl-4-*t*-butylphenyl propyl ketone (V) and 500 ml. of dry ether was added with stirring. The mixture was refluxed for 10 hr. and then was treated with water and dilute hydrochloric acid. The ether solution was washed with aqueous sodium bicarbonate, dried with anhyrous magnesium sulfate, and distilled. A fraction boiling at 125–140° (2 mm.) solidified in the receiver and weighed 200 g. (67%), white orthorhombic crystals, m.p. 61–62° (67–67.5° after recrystallization from methanol).

Anal. Calcd. for $C_{16}H_{26}O$: C, 82.05; H, 11.11. Found: C, 81.89; H, 11.08.

1-(2,6-Dimethyl-4-*t*-butylphenyl)-1-butene (VII).—A mixture of 198 g. (0.85 mole) of crude 2,6-dimethyl-4-*t*-butylphenylpropylcarbinol (VI), 129 ml. of *p*-xylene, and 1.5 g. of anhydrous copper sulfate was heated under reflux in an apparatus with a Dean–Stark trap for collection and measurement of the water produced. After 9.6 ml. of water had been collected, water production appeared to stop. The reaction mixture was cooled, washed with water and sodium bicarbonate solution, dried with anhydrous calcium chloride, and distilled. A fraction boiling at 108–128° at 1 mm. weighed 151.5 g. (0.70 mole, 82%). (The less than quantitative yield of water may have been due to some dehydration of the alcohol during its preparation and distillation.) A fraction boiling at 117–119° (1 mm.) was taken for analysis.

Anal. Calcd. for $C_{16}H_{24}$: C, 88.87; H, 11.12. Found: C, 88.84; H, 11.08.

2,6-Dimethyl-4-*t*-butyl-*n*-butylbenzene (VIII).—The 151.5-g. fraction of VII was hydrogenated without a solvent with about 3 g. of 30% palladium on charcoal as a catalyst and under 3–6 atm. of hydrogen. Vacuum distillation gave 136 g. (0.63 mole,

---

(10) All microanalyses were by Dr. Carl Tiedcke, Laboratory of Microchemistry, Teaneck, N. J.

90%) of product boiling at 109–118° (1 mm.). A fraction boiling at 116–118° (1 mm.) was taken for analysis.

Anal. Calcd. for $C_{16}H_{26}$: C, 88.07; H, 11.93. Found: C, 87.76; H, 12.01.

2,6-Dimethyl-*n*-butylbenzene (IV).—A mixture of 133 g. (0.61 mole) of 2,6-dimethyl-4-*t*-butyl-*n*-butylbenzene (VIII), 475 g. (6.1 moles) of benzene, and 12.3 g. of anhydrous aluminum chloride was stirred at 0° for 0.5 hr. The resulting deep red solution was treated with ice and water, washed with cold water and sodium bicarbonate solution, dried with calcium chloride, and distilled. Material boiling at 113–117° (17 mm.) weighed 70.0 g. (0.43 mole, 68%). Redistillation gave a fraction boiling at 106–108° at 13 mm., which was homogeneous by v.p.c.; $n^{25}\text{D}$ 1.4995.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.88; H, 11.12. Found: C, 88.89; H, 11.03.

In the infrared spectrum, out-of-plane deformations of the three adjacent ring hydrogens appeared at 769 (s) and 727 cm.$^{-1}$ (m). An additional band at 740 cm.$^{-1}$ (m) is probably due to the *n*-butyl group. The ring C═C stretching vibration had shifted to lower frequencies, as is characteristic for vicinal aromatic trisubstitution, and appeared at 1595 cm.$^{-1}$ (m).[11]

Synthesis of Infrared Spectrophotometric and Gas Chromatographic Standards.—In addition to 3,5-dimethyl-*t*-butylbenzene (III) ($n^{25}\text{D}$ 1.4940), the following isomers of IV were synthesized as infrared spectrophotometric and gas chromatographic standards.

2,4-Dimethyl-*n*-butylbenzene.[3]—*m*-Xylene was acylated with *n*-butyric anhydride and the resulting 2,4-dimethylphenyl *n*-propyl ketone was reduced by the Wolff–Kishner method, as modified by Huang-Minlon,[12] in 75% yield.

2,4-Dimethyl-*sec*-butylbenzene.—*m*-Xylene was acylated with propionyl chloride to 2,4-dimethylphenyl ethyl ketone. Reaction of this with methylmagnesium iodide gave methylethyl-2,4-dimethylphenylcarbinol. The latter was dehydrated ($CuSO_4$, boiling *m*-xylene) to 2-(2,4-dimethylphenyl)-*x*-butene, which was hydrogenated (palladium on charcoal); $n^{25}\text{D}$ 1.4999.

3,5-Dimethyl-*n*-butylbenzene.—Dilute nitric acid oxidation of mesitylene furnished 3,5-dimethylbenzoic acid, which with thionyl chloride gave 3,5-dimethylbenzoyl chloride. Reaction with di-*n*-propylcadmium gave 3,5-dimethylphenyl *n*-propyl ketone. Reduction of the latter with lithium aluminum hydride gave *n*-propyl-3,5-dimethylphenylcarbinol. Dehydration ($CuSO_4$, boiling xylene) gave 1-(3,5-dimethylphenyl)-1-butene, which was hydrogenated.

3,5-Dimethyl-*sec*-butylbenzene.—Reaction of 3,5-dimethylbenzoyl chloride with diethylcadmium gave ethyl 3,5-dimethylphenyl ketone, which with methylmagnesium iodide gave methylethyl-3,5-dimethylphenylcarbinol and thence its dehydration product, 2-(3,5-dimethylphenyl)-*x*-butene, which was hydrogenated; $n^{25}\text{D}$ 1.4939.

2,5-Dimethyl-*n*-butylbenzene.—*p*-Xylene was acylated with *n*-butyric anhydride and the resulting 2,5-dimethylphenyl *n*-propyl ketone was reduced by the Wolff–Kishner method, as modified by Huang-Minlon,[12] in 80% yield; $n^{25}\text{D}$ 1.4959.

All these compounds were homogeneous by v.p.c.

Isomerizations.—Isomerization of 2,6-dimethyl-*n*-butylbenzene was carried out as described previously[2,3] by heating it 3.5 hr. on a steam bath with about 22% of its weight of anhydrous aluminum chloride. It was washed free of aluminum chloride, dried with calcium chloride, and distilled under reduced pressure. A fraction distilling to 132° at 17 mm. comprised 71% by weight of the recovered material and a higher boiling residue, 29%.

2,4-Dimethyl-*n*-butylbenzene (14.40 g.) was heated 3.5 hr. on a steam bath with 2.50 g. of anhydrous aluminum chloride, washed, dried, and distilled at reduced pressure. There was obtained 8.70 g. distilling to 132° at 17 mm. and 3.31 g. of a higher boiling residue.

Analyses.—Careful gas–liquid chromatographic analyses were performed on the volatile isomerisates. A Loenco Model 70 Hi-Flex dual-column chromatograph was used. Three-meter columns of silicone 710 oil on firebrick were operated isothermally at 175°. Retention times were obtained for all available standards and were reproducible.

At least 17 components were revealed in the isomerisate from 2,6-dimethyl-*n*-butylbenzene, as shown in Table I. Most of the same components appeared to be present in the isomerisate from 2,4-dimethyl-*n*-butylbenzene, and in approximately the same proportions, except that the percentage conversion appeared to be smaller in the latter case.

Infrared spectra of the two isomerisates were obtained, but were too complex for detailed analysis. They indicated, however, that no significant amount of compounds with tertiary hydrogen (*sec*-butyl groups) were present.

Time Study.—A mixture of 0.7474 g. of 2,6-dimethyl-*n*-butylbenzene, 0.0311 g. of tetrachloroethylene, and 0.1335 g. of anhydrous aluminum chloride was placed in a vial, sealed with a serum cap, and placed in a constant-temperature bath at 100°. Samples were withdrawn periodically with a hypodermic syringe and injected into a Loenco Model 70 Hi-Flex dual-column gas chromatograph with columns of silicone 710 oil on firebrick. The temperature was programmed from 100 to 200° at a rate of 8°/min.

The tetrachloroethylene appeared to be unaffected. Similar-sized samples were injected and its chromatographic peak was nearly constant. A chromatograph of the original mixture of 2,6-dimethyl-*n*-butylbenzene and tetrachloroethylene gave peak areas in the ratio 25.6:1, compared with the molar ratio 24.6:1.

The factor, 25.6, was used as a multiplier of the tetrachloroethylene peak area in each sample. Peak areas of other components were reduced to a percentage of the resulting multiplication product. Results for the reaction mixture at intervals of time are shown in Table II.

Acknowledgment.—This work was supported by a grant-in-aid from the Research Committee of The City College. We are also indebted to Miss Joan Frank and Faberge, Inc., for some of the infrared spectra, to Brookhaven National Laboratory for use of gas chromatographs and for infrared and n.m.r. spectra, to Mr. S. Y. Wong and the University of Southern California for an n.m.r. spectrum of 1,2,4-trimethylbenzene, and to Mr. George L. Mayers for synthesis of 2,5-dimethyl-*n*-butylbenzene.

---

[11] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 71–79.

[12] Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).