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Alkylbenzenes. XIV. Diphenylalkanes as Intermediates in Fragmentation, Rearrangement, and Disproportionation Reactions of Alkylbenzenes¹

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Diphenylalkanes have been identified among the products of reaction of propyl- and butylbenzenes with aluminum chloride. These diphenylalkanes are those expected as by-products of dealkylations and as intermediates in fragmentations according to mechanisms proposed in a recent publication. Provision of an active hydride abstractor (*t*-butylcarbonium ion from *t*-butyl chloride, aluminum chloride, and benzene) facilitated the production of these diphenylalkanes at lower temperatures. When treated under the same experimental conditions, diphenylalkanes gave the same fragmentation products as the alkylbenzenes from which they are expected as intermediates. Rearrangements and dealkylations produced by reaction of the diphenylalkanes with aluminum chloride at room temperature were studied. A mechanistic scheme which correlates the dealkylations, fragmentations, rearrangements, and disproportionations of alkylbenzenes is outlined, and the significance of diphenylalkanes as intermediates and by-products of these reactions is emphasized.

In a recent publication⁴ we reported the isolation of *meso*-2,3-diphenylbutane from a reaction in which *sec*-butylbenzene was heated with aluminum chloride; we suggested that diphenylbutanes are by-products of dealkylation reactions and intermediates in fragmentation reactions of alkylbenzenes. In the present article we report further evidence of intervention of these intermediates in fragmentation reactions and first experimental evidence that they are also intermediates in the rearrangements of alkylbenzenes which have been observed. We shall show that it is now possible to correlate nicely mechanisms of dealkylation, fragmentation, and rearrangement and the mechanism of disproportionation that has been shown to involve diphenylalkane intermediates.⁵

Results and Discussion

Detection and Production of Diphenylbutanes.—

The isolation of *meso*-2,3-diphenylbutane was realized owing to the fortuitous circumstance of its high melting point and its low solubility in the reaction mixture which contained it in very small amount. A number of other diphenylbutanes have now been detected by vapor-phase chromatography as minor components of the complex mixtures produced by heating different butylbenzenes with aluminum chloride at 100°. From the reaction of *sec*-butylbenzene, we identified *dl*-2,3-diphenylbutane, as well as *meso*-2,3-diphenylbutane, 1,2-diphenyl-2-methylpropane, and 2,2-diphenylbutane; from isobutylbenzene: *dl*- and *meso*-2,3-diphenylbutane and 1,2-diphenyl-2-methylpropane; from *t*-butylbenzene: 1,2-diphenyl-2-methylpropane and 1,1-diphenyl-2-methylpropane; from *n*-butylbenzene: 1,2- and 1,3-diphenylbutane. Extensive fragmentation of the butylbenzenes occurred, as described in the previous publication.

2,2-Diphenylbutane is the other isomer expected as a by-product of dealkylation of *sec*-butylbenzene according to the mechanism proposed previously.⁶ It was found in a reaction mixture after heating for 0.5 hr. at 100°; it was missing from a reaction mixture which had been heated 2 hr. 1,2-Diphenyl-2-methylpropane

was found in larger amount in the 2-hr. reaction mixture; it was expected in view of the known interconversion of *sec*-butylbenzene and isobutylbenzene. For the same reason, 2,3-diphenylbutanes were also expected from isobutylbenzene. 1,2-Diphenyl-2-methylpropane was also expected from *t*-butylbenzene; 1,1-diphenyl-2-methylpropane is produced by rearrangement, as is described below. No diphenylbutanes were produced from *n*-butylbenzene in 0.5 hr. and there was virtually no dealkylation or fragmentation; after a 3-hr. heating period, some dealkylation and fragmentation had occurred, and traces of the diphenylbutanes were detected.

As described in the previous article,⁵ the step leading directly to diphenylalkanes is thought to be one in which a carbonium ion abstracts a hydride ion from the side chain of the alkylbenzene, producing a molecule of alkane and a phenylalkylcarbonium ion. This ion then alkylates benzene to give the diphenylalkane. The structure of the alkyl side chain of an arene might be expected to affect this process in two ways: (1) the degree of substitution on the α -carbon should determine the stability of the alkylcarbonium ion produced in the fission step; (2) the degree of substitution of the other carbon atoms, as well as that of the α -carbon atom, should determine the ease of hydride abstraction. Thus, although *t*-butylbenzene should give a stable tertiary carbonium ion in the fission step, abstraction of hydride from the primary carbons of the *t*-butyl group should be difficult. *sec*-Butylbenzene should give a secondary carbonium ion in the fission step, but hydride abstraction from the tertiary α -carbon should be easy. Examination of Table I of a previous article⁴ reveals that *sec*-butylbenzene actually gives more extensive fragmentation than *t*-butylbenzene (although dealkylation of *t*-butylbenzene is much more extensive; the dealkylation is discussed further below). *n*-Butyl- and *n*-propylbenzene gives lower yields of fragmentation products than their isomers, and ethylbenzene, which cannot rearrange to an isomer having a tertiary side chain carbon, gives no fragmentation under the conditions described. These facts lend support to the theory of intermediate formation of diphenylalkanes in the fragmentation reactions of alkylbenzenes.

On the assumption that a good carbonium ion source (hydride abstractor) should augment the production of diphenylalkanes from alkylbenzenes, we treated a number of butylbenzenes with *t*-butyl chloride and

(1) Presented in part in a lecture at Rice University, Houston, Texas, Dec. 17, 1963.

(2) Robert A. Welch Foundation Predoctoral Fellow, 1963-1964.

(3) Jefferson Chemical Co. Fellow, 1962-1963.

(4) R. M. Roberts, E. K. Baylis, and G. J. Fonken, *J. Am. Chem. Soc.*, **85**, 3454 (1963).

(5) A. Streitwieser, Jr., and L. Reif, *ibid.*, **82**, 5003 (1960).

(6) See Fig. 1 in ref. 4.

aluminum chloride in benzene solution.⁷ At 5° for about 1 hr., *sec*-butylbenzene gave a 6% yield of diphenylbutanes, consisting of 2,2-diphenylbutane (mainly) and *dl*- and *meso*-2,3-diphenylbutane.⁸ At 25°, about a 40% yield of diphenylbutanes was produced, which consisted of *dl*- and *meso*-2,3-diphenylbutane (mainly) and 1,2-diphenyl-2-methylpropane. Isobutylbenzene treated similarly gave about a 42% yield of diphenylbutanes at 5° and about 50% at 25°, consisting in both experiments of a 2:1 ratio of 1,2-diphenyl-2-methylpropane and 1,1-diphenyl-2-methylpropane, with traces of *dl*- and *meso*-2,3-diphenylbutane. *t*-Butylbenzene, after similar treatment at 25°, gave about a 2% yield of diphenylbutanes, consisting of about a 3:1 ratio of *dl*- and *meso*-2,3-diphenylbutane to 1,2-diphenyl-2-methylpropane. *n*-Butylbenzene, after similar treatment at 25°, gave about a 1% yield of diphenylbutanes, mainly 1,2-diphenylbutane, with very small amounts of 1,1- and 1,3-diphenylbutane. Thus, the extent to which *sec*-butyl- and isobutylbenzene were converted to diphenylbutanes was significantly greater than that of *t*-butyl- and *n*-butylbenzene, in keeping with the greater extent of fragmentation of the first two isomers. The diphenylbutanes produced in these experiments were the same ones found among the fragmentation products from reactions at higher temperatures in the absence of *t*-butyl chloride.

Fragmentation of Diphenylbutanes.—The obvious test of an intermediate is to ascertain whether or not it gives the same products as its assumed precursor under the same experimental conditions. Several of the pure diphenylbutane isomers were synthesized and treated with aluminum chloride under the same conditions which produce fragmentation of butylbenzenes. The results from some of the experiments are summarized in Table I. It may be noted that all of the expected alkylbenzenes were produced, and in approximately the same proportions as from the butylbenzenes,⁴ with the exception that the ratio of ethylbenzene to toluene was higher in the products from the diphenylbutanes. The major source of ethylbenzene is probably cleavage of *dl*- and *meso*-2,3-diphenylbutane which is produced not only directly from *sec*-butylbenzene, but also by isomerization from the other diphenylbutane isomers, as described below. Some direct cleavage of butylbenzenes (*i.e.*, not *via* diphenylbutanes) doubtless does occur without producing ethylbenzene; *e.g.*, isobutylbenzene → toluene + isopropylbenzene.

The distribution of fragmentation products from the diphenylbutanes can be rationalized quite well in terms of the mechanism proposed earlier,⁹ with the application of one or two reasonable assumptions. (1) Fissions which produce the most stable carbonium ions are favored. (2) In reactions at 70 to 100°, cleavage may occur before isomerizations of diphenylbutanes are complete, but rates of cleavage and isomerization may be of the same order (isomerization is discussed below). For this reason the diphenylbutane isomers give similar, but not identical, mixtures of fragmentation products.

(7) C. Serres and E. K. Fields, *J. Org. Chem.*, **28**, 1624 (1963).

(8) Another product detected in small yield was tentatively identified with the compound to which K. T. Serijan and P. H. Wise ascribed the structure of 1-methyl-1,3-diethyl-3-phenylhydridene [*J. Am. Chem. Soc.*, **74**, 365 (1952)]. We plan further investigation of this product.

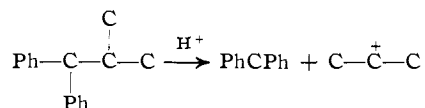
(9) See Fig. 2 of ref. 4.

TABLE I
FRAGMENTATION AND DEALKYLATION PRODUCTS FROM
DIPHENYLBUTANES^a

Diphenylbutanes	Alkylbenzenes, R-C ₆ H ₅ ^b						
	Total, % ^c	Me, % ^d	Et, % ^d	<i>n</i> - Pr, % ^d	<i>i</i> -Pr, % ^d	<i>sec</i> - Bu, % ^{d,e}	<i>i</i> -Bu, % ^{d,e}
$\begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C}' \\ \quad \\ \text{Ph} \quad \text{Ph} \\ \\ \text{Ph} \end{array}$	12	3	23	2	4		68
$\begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C} \\ \quad \\ \text{Ph} \quad \text{C} \\ \\ \text{C} \end{array}$	16	11	26	1	4	28	30
$\begin{array}{c} \text{Ph}-\text{C}-\text{C}-\text{Ph}^f \\ \quad \\ \text{C} \quad \text{C} \end{array}$	21	11	18	2	8	22	38
$\begin{array}{c} \text{C} \\ \\ \text{Ph}-\text{C}-\text{C}-\text{C} \\ \\ \text{Ph} \end{array}$	24	4	16	2	9		69

^a Reactions at 100°, 3 hr.; reactants: (Ph)₂C₆H₅, 0.10 mole; AlCl₃, 0.066 mole; H₂O, 0.033 mole. ^b Boiling range 81–176°; benzene was produced in all experiments. ^c Weight per cent of original diphenylbutane. ^d Percentage of each alkylbenzene in the mixture from v.p.c. analysis. ^e Distinction between *sec*-Bu and *i*-Bu was by infrared. ^f Experiment of Dr. G. J. Fonken on *meso* isomer; slightly smaller amount of AlCl₃ used; temperature 70°, 3 hr. ^g Contained *ca.* 20% of 1,2-diphenyl-2-methylpropane; see Experimental section.

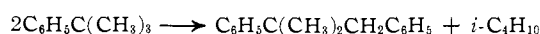
Diphenylmethane was detected among the products from 1,1-diphenyl-2-methylpropane, but not from the other isomers. This probably arises from the fission step



which results in a lower yield of toluene and a higher yield of isopropylbenzene than from the other diphenylbutanes.

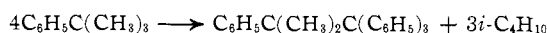
The alkane mixtures produced from the diphenylbutanes were quite different both in amount (smaller) and in composition from those evolved from the butylbenzenes, as might be expected. The major alkane from all of the diphenylbutane isomers was isobutane, and isopentane was found in larger amount than *n*-butane. It is quite likely that the isopentane arises from unsymmetrical cleavage of an octane isomer, which is formed from addition of *t*-butylcarbonium ion to isobutylene followed by hydride exchange. Experiment confirmed that when 2,2,3-trimethylpentane was heated with aluminum chloride at 70°, an alkane mixture was evolved which proved to be 90% isobutane and 10% isopentane. Small amounts of compounds having retention times corresponding to octane isomers were detected among the products from several of the fragmentation reactions.

The very extensive dealkylation of *t*-butylbenzene deserves mention in connection with the production of diphenylalkanes. Applied to *t*-butylbenzene, the mechanism proposed in Fig. 1 of a previous article⁴ would give the stoichiometry



i.e., a maximum 50 mole % yield of isobutane from *t*-butylbenzene. Yet 70–75 mole % yields of isobutane

are frequently realized.⁴ It is interesting to speculate that further hydride abstraction from 1,2-diphenyl-2-methylpropane may occur; hydride abstraction from the methylene carbon should be much easier than from *t*-butylbenzene. Formation of 1,1,1,2-tetraphenyl-2-methylpropane would give a 75 mole % yield of isobutane from *t*-butylbenzene.



The tetraphenylbutane may then undergo further dealkylation and fragmentation.

Rearrangements of Diphenylalkanes.—The ease of interconversion of diphenylbutane isomers was investigated. Isomerization of 1,2-diphenyl-2-methylpropane and of *dl*-2,3-diphenylbutane to *meso*-2,3-diphenylbutane by aluminum chloride at room temperature has been described.¹⁰ When we repeated the preparation of this diphenylbutane by the two methods used by these workers (both of which involved aluminum chloride), we found the products to consist of four isomers. Somerville and Spoerri recognized the presence of *meso*-2,3-diphenylbutane in their products and separated it by chilling the mixture and filtering off the crystalline isomer. We found (by v.p.c. analysis) that the filtrate, which they assumed to be pure 1,2-diphenyl-1-methylpropane, contained small amounts of *dl*-2,3-diphenylbutane and up to ca. 30% of 1,1-diphenyl-2-methylpropane. After several other attempted syntheses which resulted in mixtures of isomers, we finally succeeded in preparing pure specimens of 1,2-diphenyl-2-methylpropane, 1,1-diphenyl-2-methylpropane, and 2,2-diphenylbutane.¹¹ The products were demonstrated pure by v.p.c. and infrared analysis and their n.m.r. spectra were in accord with the assigned structures.

Treatment of either 1,2-diphenyl-2-methylpropane or 1,1-diphenyl-2-methylpropane with aluminum chloride at room temperature for 4 hr. produced a mixture containing both isomers in a ratio of about 2:1; *dl*- and *meso*-2,3-diphenylbutane were also produced in smaller amounts. These isomerizations may be described by means of the scheme outlined in Fig. 1. 1,2-Diphenyl-2-methylpropane (VI) is converted to 1,1-diphenyl-2-methylpropane (III) *via* carbonium ions VII and IV by hydride exchange and a 1,2-phenyl shift and/or by dealkylation and realkylation *via* V, I, and II. Isobutylbenzene (I) was found among the products. The reactions are reversible of course; from the equilibrium composition, VI appears to be more stable than III. Somerville and Spoerri¹⁰ proposed that the conversion of VI to X occurred *via* dealkylation of VI to V, followed by a 1,2-hydride shift to II, a 1,2-methyl shift to IX, and realkylation to 2,3-diphenylbutane (X). We consider the route VI \rightarrow VII \rightarrow XI \rightarrow X more likely in this case because the two intermediate carbonium ions are of lower energy than IX. Treatment of *meso*-2,3-diphenylbutane (X) with aluminum chloride at room temperature for 4 hr. gave partial isomerization to the *dl* isomer and, to a smaller extent, to VI; no XIII was found, in keeping with the expected greater difficulty of passing through the higher energy ion XIV (about equivalent to IX). 2,2-Diphenylbutane (XIII) was

partially isomerized in 4 hr. at room temperature to *dl*- and *meso*-2,3-diphenylbutane (X); considerable dealkylation to *sec*-butylbenzene (VIII) occurred. Longer treatment (24 hr.) at room temperature produced mainly more dealkylation.

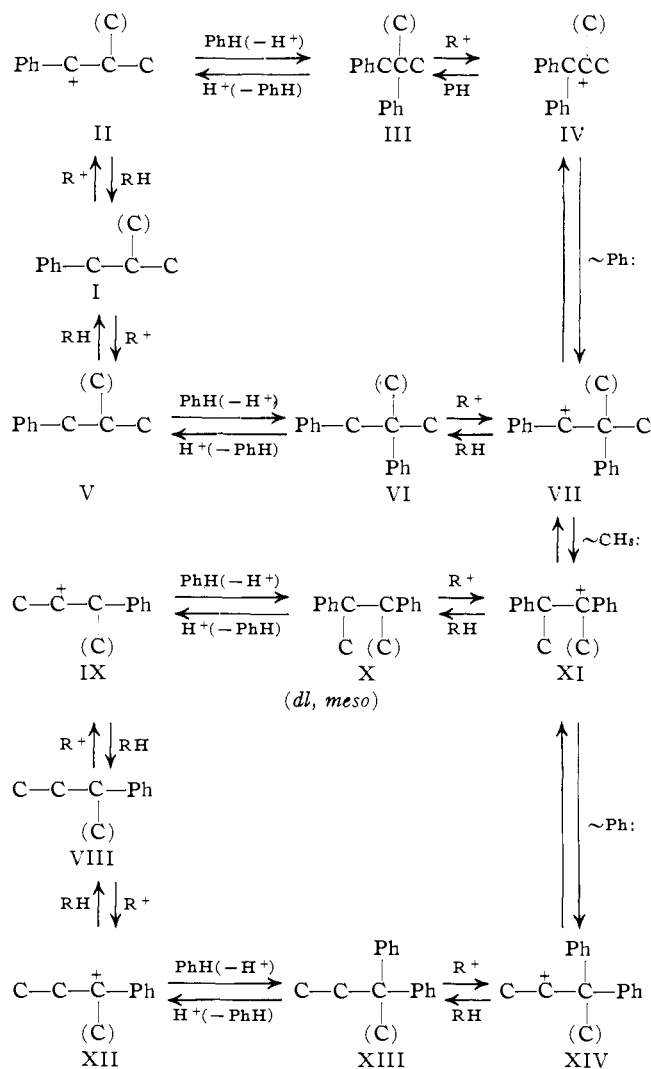


Figure 1.

Mechanism of Rearrangement of Butylbenzenes and Propylbenzenes.

Remembering that heating all of the four diphenylbutane isomers (III, VI, X, and XIII) at 70 to 100° with aluminum chloride produces both *sec*- and isobutylbenzene (I and VIII) and that these same butylbenzene isomers are interconverted by similar treatment leads to the conclusion that the pathways of Fig. 1 represent a very reasonable mechanism for the interconversion of the butylbenzenes, as well as of the diphenylbutanes. It appears more satisfactory than the mechanism proposed previously¹² in that no primary carbonium ions appear as intermediates.¹³ The identification of the diphenylbutanes produced from *sec*-butyl- and isobutylbenzene by heating with aluminum chloride fit well into this mechanism. For example, the finding of XIII from a 0.5-hr. reaction of *sec*-butylbenzene, but not from a 2-hr. reaction, is indicative of facile alkylation to XIII *via* XII, but also of

(10) W. T. Somerville and P. E. Spoerri, *J. Am. Chem. Soc.*, **74**, 3803 (1952).

(11) These syntheses, as well as certain interesting aspects of rearrangements observed in the unsuccessful syntheses, will be described separately.

(12) (a) R. M. Roberts, Y. W. Han, C. H. Schmid, and D. A. Davis, *J. Am. Chem. Soc.*, **81**, 640 (1959); (b) J. E. Douglass and R. M. Roberts, *J. Org. Chem.*, **28**, 1229 (1963).

(13) G. J. Karabatsos and F. M. Vane, *J. Am. Chem. Soc.*, **85**, 729 (1963).

facile dealkylation. Alkylation to X *via* XI is slower but X is more stable than XIII, hence dealkylation is also slower.

Analogy between interconversion of *sec*-butyl- and isobutylbenzene and of α - and β -C¹⁴-labeled *n*-propylbenzene has been pointed out before. It is obvious that a mechanism analogous to that of Fig. 1, involving diphenylpropane intermediates, may be written. In fact, if the carbon atoms which are enclosed in parentheses are considered to label the carbon atoms to which they are attached in the same way as C¹⁴ isotopic atoms would, the mechanism may easily be seen to apply directly to the propylbenzene rearrangement. Here too it will be found that no primary carbonium ions are involved.¹³

The results of their ingenious experiments on transalkylation (disproportionation) of ethylbenzene gave Streitwieser and Reif⁵ compelling evidence of diphenylalkanes as intermediates in such reactions of primary alkylbenzenes. The facility of alkylation-dealkylation steps implied by this work led them independently to propose a mechanism for the isotopic *n*-propylbenzene rearrangement identical with that outlined in Fig. 1 (with the exception that the routes involving the 1,1-diphenylpropanes were not included).¹⁴

We now have evidence supporting this mechanism for propylbenzene rearrangement. Some of it is of the same type as for the butylbenzenes. 1,2-Diphenylpropane was detected by v.p.c. among the products of reactions in which *n*-propyl- α -C¹⁴-benzene was isomerized to *n*-propyl- β -C¹⁴-benzene by aluminum chloride at 80 to 100°.

In a series of experiments, the molar ratio of labeled propylbenzene:aluminum chloride:water was kept constant (3:1:0.25) and initial benzene:*n*-propylbenzene ratios of 0, 1, 2, and 4 were used. The mixtures were stirred and heated for 6.5 hr.; although we intended the reaction temperatures to be the same, they varied from 87 ± 1° in the reaction with no added benzene to 83 ± 1° in the reaction with the largest amount of added benzene. The extents of rearrangement of C¹⁴ from the α -carbon were (for the reactions with benzene:propylbenzene ratios of 0, 1, 2, and 4): 22.7 ± 0.5, 38.7 ± 0.5, 44.3 ± 0.2, and 49.9 ± 0.3%. It is noteworthy that the last experiment represents the first complete equilibration of the α - and β -carbon atoms of *n*-propylbenzene by a single treatment with aluminum chloride or any other Lewis acid catalyst.¹⁵ The marked increase in the extent of rearrangement with increasing amounts of benzene may be ascribed to two factors. High initial benzene concentrations will reduce the formation of polyalkylbenzenes by disproportionation, which should result in less deactivation of the catalyst.¹⁵ However, the concentration of the catalyst was much lower in the mixtures containing more benzene, which should reduce its effectiveness. It is difficult to assess the relative influence of these opposing effects.

The second factor which may have led to more rearrangement in the benzene solutions is the actual participation of benzene in the reaction to produce diphenylpropanes, which are very probably intermediates in the rearrangement.

Production of diphenylpropanes from *n*-propylbenzene even at 0° was demonstrated by using the *t*-butyl chloride technique described above with the butylbenzenes. A 76% yield of diphenylpropanes was obtained, consisting of a 2:1 ratio of 1,2-diphenylpropane to 1,1-diphenylpropane.

1,2-Diphenylpropane was shown to undergo dealkylation and cleavage as expected upon heating with aluminum chloride; *n*-propylbenzene and isopropylbenzene, ethylbenzene, and toluene were produced in about the same proportions as when *n*-propylbenzene was the starting material,⁴ except that the amount of ethylbenzene was high, as was found in the diphenylbutane fragmentations.

An interesting aspect of the rearrangements which has not yet been discussed in this article is the extent of rearrangement of *sec*-butylbenzene and isobutylbenzene to *t*-butylbenzene, and of *n*-propylbenzene to isopropylbenzene. In recent publications,^{4,12b} we have ascribed the minor extents of these rearrangements observed to the greater susceptibility of *t*-butylbenzene and isopropylbenzene to dealkylation. It is difficult to determine exactly how much of these isomers may be formed and lost through dealkylation. We are re-examining this question in the light of the probability that the major rearrangements occur *via* diphenylalkane intermediates. It is interesting to note that none of the diphenylalkanes pictured in Fig. 1 can dealkylate to *t*-butylbenzene or isopropylbenzene except through the intermediate formation of a *primary* carbonium ion. It now seems possible that indeed only small amounts of these alkylbenzenes are produced, and that this may be attributed to the high energy of primary carbonium ion intermediates.¹³

In a previous article^{12b} we concluded that the distribution of C¹⁴ found in isopropylbenzene derived from *n*-propyl- α -C¹⁴-benzene supported the mechanism outlined in that article. It is comforting to note that the experimental data on which those conclusions were based support equally well the diphenylalkane intermediate mechanism, which we now feel rests on a rather broad base of experimental evidence.

Experimental

Materials.—All of the diphenylbutane and diphenylpropane isomers have been reported previously. The methods reported for synthesis of 1,2-diphenyl-2-methylpropane¹⁰ did not give a pure product. Our successful method will be published separately.¹¹ All synthetic products and commercial starting materials were checked for purity by vapor-phase chromatography (v.p.c.) and infrared analysis. Aluminum chloride used was commercial anhydrous sublimed reagent grade.

Analytical Procedures.—Identification of the diphenylbutane and diphenylpropane isomers required use of three different v.p.c. columns, since there was overlap of retention time by some of the isomers on any one column. The columns used were (1) 6-ft., 30% Carbowax-1000 on 60/80 mesh firebrick; (2) 12-ft., 30% silicone gum rubber SE-30 on 42/60 mesh firebrick; (3) 12-ft., 5% Bentone-34 and 5% silicone SE-52 on 60/80 mesh Chromosorb-W. The columns were operated at 160, 190, or 220° in a Beckman GC-2A instrument. A Beckman IR-5A was used for infrared analysis. A Varian A-60 spectrometer was used for n.m.r. analysis.

Radioassays were performed with a Packard Tri-Carb Model 314EX scintillation spectrometer.

Fragmentation of butylbenzenes was carried out as described previously.⁴ After decomposition with water and the usual extraction treatment, the reaction mixtures were distilled under atmospheric pressure through an 80-cm. Nichrome spiral column. A fraction boiling between 81 and 176° was usually collected. The residue was then distilled under vacuum; a fraction boiling

(14) A. Streitwieser, Jr., and L. Reif, *J. Am. Chem. Soc.*, **86**, 1988 (1964).

(15) R. M. Roberts and J. E. Douglass, *J. Org. Chem.*, **28**, 1225 (1963).

at about 100–132° (2 mm.) was collected. The distillation fractions were examined by v.p.c. The 81–176° fractions were found to be mixtures of alkylbenzenes similar to those reported previously.⁴ The diphenylbutanes found in the vacuum-distilled fractions are described in the Results and Discussion section.

Treatment of Butylbenzenes with *t*-Butyl Chloride, Benzene, and Aluminum Chloride at Low Temperatures.—The butylbenzene (0.25 mole), benzene (1.25 mole), and aluminum chloride (0.025 mole) were stirred (at 5 or 25°) while the *t*-butyl chloride (1.00 mole) was added dropwise during 0.5 hr. The reaction mixture was allowed to stir at the same temperature for an additional 45 min. It was then decomposed with water, washed, dried, and distilled at atmospheric pressure up to the boiling point of the dibutylbenzenes (230–240°). The residue was analyzed by v.p.c. for the diphenylbutanes. Data are given in Results and Discussion section.

Fragmentation of the Diphenylbutanes.—These were carried out in the same apparatus and in the same way as in the case of the butylbenzenes.⁴ Gases evolved were collected as before and analyzed by v.p.c. Details and results are given in Table I. The data given on 1,2-diphenyl-2-methylpropane was from an experiment in which a product containing about 20% 1,1-diphenyl-2-methylpropane was the starting material. When pure 1,2-diphenyl-2-methylpropane was obtained later on, it was subjected to the same treatment and gave essentially the same mixture of products. (It was known earlier that the two isomers were rapidly interconverted by aluminum chloride.)

Many experiments were performed on three of the isomers (2,2-diphenylbutane, 1,2-diphenyl-2-methylpropane, and 1,1-diphenyl-2-methylpropane) in which the heating periods were shorter (5 min. to 2 hr.) and the products were analyzed. Interesting changes in the products with time were noted. (1) More isobutane and less isopentane were produced in the early reaction stages from all three diphenylbutanes. (2) Traces of *t*-butylbenzene were produced by all three isomers in the early stages. (3) Branched-chain octanes were identified as products from all three isomers after short reaction times. (4) The ratio of isobutylbenzene:*sec*-butylbenzene produced from 1,2-diphenyl-2-methylpropane decreased from 73:27 (5-min. reaction) to 47:53 (3 hr.). The ratio produced from 1,1-diphenyl-2-methylpropane (ca. 65:35) did not change much with time. The ratio produced from 2,2-diphenylbutane changed from 5:95 (5 min.) to 50:50 (3 hr.). (5) The production of isopropylbenzene from 1,1-diphenyl-2-methylpropane was much higher at first.

Rearrangements of Diphenylbutanes.—In the following experiments, the reactants were mixed in the proportions diphenylbutane (1 mole), benzene (10 moles), aluminum chloride (0.1 mole), and stirred magnetically for 4 hr. at 25°. The reaction mixture was decomposed with water, washed, dried, and distilled at atmospheric pressure to separate benzene and other alkylbenzenes with boiling points up to those of the butylbenzenes. The residue was chilled to –5° to crystallize *meso*-2,3-diphenylbutane, which was separated by filtration. The filtrate was analyzed by v.p.c. and/or distilled under vacuum. Distillates were further analyzed by v.p.c., infrared, and n.m.r. spectrometry. Results from four diphenylbutanes are given below.

1,2-Diphenyl-2-methylpropane (21 g., 0.10 mole) gave 0.43 g. (3.1 mole %, based on starting material) of butylbenzene, mostly isobutylbenzene (minor amount of *sec*-butylbenzene), traces of isopropylbenzene, ethylbenzene, and toluene. Chilling the residue gave 2.6 g. (12 mole %) of *meso*-2,3-diphenylbutane. The filtrate (14.2 g.) was 90% diphenylbutanes; it contained 1,2-diphenyl-2-methylpropane (38 mole %), 1,1-diphenyl-2-methylpropane (18 mole %), and *dl*-2,3-diphenylbutane (5 mole %).

1,1-Diphenyl-2-methylpropane (10.5 g., 0.050 mole) gave 1.1 g. (16 mole %) of butylbenzene, mostly isobutylbenzene (minor amount of *sec*-butylbenzene), 0.38 g. (6 mole %) of isopropylbenzene, and traces of ethylbenzene. The residue from the distillation gave no *meso*-2,3-diphenylbutane when cooled; further distillation gave 6.4 g. of a fraction boiling at 284–296°. This fraction was found to contain diphenylmethane (2.5 mole %), 1,2-diphenyl-2-methylbutane (41 mole %), and 1,1-diphenyl-2-methylbutane (18 mole %).

A smaller sample of 1,1-diphenyl-2-methylpropane stirred for 24 hr. at 25° with the same proportions of benzene and aluminum chloride gave a mixture which was analyzed by v.p.c. only. It was very similar to that from the 4-hr. experiment except that the dealkylation to *sec*-isobutylbenzene was higher (ca. 28 mole %).

meso-2,3-Diphenylbutane (10.5 g., 0.050 mole) gave 0.30 g. (4.5 mole %) of butylbenzene, mostly *sec*-butylbenzene (minor

amount isobutylbenzene), traces of isopropylbenzene, ethylbenzene, and toluene. The chilled residue gave 7.0 g. (67 mole %) of *meso*-2,3-diphenylbutane. The filtrate (1.7 g.) contained *dl*-2,3-diphenylbutane (11 mole %), 1,2-diphenyl-2-methylpropane (4 mole %), and 1,3-diphenylbutane (2 mole %).

2,2-Diphenylbutane (10.5 g., 0.050 mole) gave 0.57 g. (8.5 mole %) of *sec*-butylbenzene. The chilled residue gave 2.6 g. (25 mole %) of *meso*-2,3-diphenylbutane. The filtrate was distilled to give 5.8 g., b.p. 150–160° (20 mm.); this fraction contained 2,2-diphenylbutane (45 mole %) and *dl*-2,3-diphenylbutane (10 mole %).

Treatment of 2,2-diphenylbutane with *t*-butyl chloride, benzene, and aluminum chloride as described above converted it into a mixture of *meso*-2,3-diphenylbutane (49%), *dl*-2,3-diphenylbutane (18%), 1,2-diphenyl-2-methylpropane (18%), and 2,2-diphenylbutane (15%).

Rearrangements of *n*-Propyl- α -C¹⁴-benzene. A. Effect of Benzene Concentration on Extent of Rearrangement.—*n*-Propyl- α -C¹⁴-benzene was synthesized as described previously.¹⁵ In this series of experiments, the molar proportion of *n*-propyl- α -C¹⁴-benzene:aluminum chloride:water was 3:1:0.25 and the benzene-*n*-propyl- α -C¹⁴-benzene molar proportions were 0, 1, 2, and 4. The amounts of *n*-propyl- α -C¹⁴-benzene used in these experiments ranged from 13 g. (benzene-propylbenzene = 0 expt.) to 3 g. (benzene-propylbenzene = 4 expt.) so that the over-all volumes were comparable. Reactions were carried out by mixing the components at room temperature with stirring and then immersing the reaction flask in an oil bath at 85–88°. Stirring was continued for 6.5 hr. The temperature of the reaction mixture was determined by a thermometer in a well immersed in the reaction mixture. The average temperatures for the 0, 1, 2, and 4 benzene-propylbenzene reactions were 87 ± 1, 85 ± 1, 83 ± 1, and 83 ± 1°, respectively.

The reaction mixtures were decomposed with water and worked up in the usual way. Propylbenzene was recovered by distillation through a micro spiral wire column 15 cm. long, and its purity was confirmed by v.p.c. analysis (2–4% isopropylbenzene was present). It was degraded to benzoic acid in the usual way. This was recrystallized, sublimed twice, and radioassayed.

The benzoic acid from the starting material had 1064 ± 1 d.p.m./mg. The samples from the reactions had (benzene:propylbenzene = 0, 1, 2, 4): 823 ± 5, 652 ± 4, 593 ± 1, and 533 ± 1 d.p.m./mg., corresponding to 22.7 ± 0.5, 38.7 ± 0.5, 44.3 ± 0.2, and 49.9 ± 0.3% rearrangement of C¹⁴ from the α -carbon.

B. Detection of 1,2-Diphenylpropane.—In several experiments similar to those of the above series, 1,2-diphenylpropane was identified among the high-boiling products of the reactions by v.p.c. These reaction mixtures were heated 2 hr. at 83 to 100°. Rearrangements of C¹⁴ from the α - to β -carbons of the side chain of from 17 to 32% occurred. Yields of 1,2-diphenylpropane of about 1%, based on *n*-propyl- α -C¹⁴-benzene, were estimated from v.p.c. analysis. The 1,2-diphenylpropane was identified by comparison of its retention times on the three different columns described above with those of authentic material (see below). No 1,1-diphenylpropane was found.

Treatment of *n*-Propylbenzene with *t*-Butyl Chloride, Benzene, and Aluminum Chloride at Low Temperature.—*n*-Propylbenzene was treated at 0° in the same way as the butylbenzenes (described above). Besides *t*-butylbenzene and *di-t*-butylbenzene, a 76% yield of diphenylpropanes was obtained; it consisted of a 2:1 mixture of 1,2-diphenylpropane and 1,1-diphenylpropane.

Fragmentation of 1,2-Diphenylpropane.—This hydrocarbon was synthesized from phenyl-2-propanone by reaction with phenylmagnesium bromide, followed by dehydration of the carbinol and hydrogenation (Pd–C) of the alkene.

A 27.3-g. (0.140 mole) sample was heated at 100° for 6.5 hr. with 6.18 g. (0.0463 mole) of aluminum chloride and 0.21 g. (0.012 mole) of water. After the usual treatment, the reaction mixture was found by v.p.c. to contain alkylbenzenes in the following relative mole percentages: toluene (1.1), ethylbenzene (10.9), *n*-propylbenzene (87.5), and isopropylbenzene (0.5). The *n*-propylbenzene represented 27 mole % of the whole complex mixture. Other identified liquid products were butylbenzenes, branched-chain hexylbenzenes, and diphenylmethane.

The gas evolved contained about 80% isobutane, and 20% propane.

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