New Friedel-Crafts Chemistry. XVII. Synthesis of Some Pure Di- and Triphenylalkanes. Identification of By-products from Carbonium Ion Processes

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Synthetic procedures are described for obtaining the following di- and triphenylbutanes in a state of high purity: 1,1-, 1,2-, 1,3-, and 2,2-diphenylbutane; DL- and *meso*-2,3-diphenylbutane; 1,1-diphenyl-2-methylpropane and 1,2-diphenyl-2-methylpropane; and 2-methyl-1,1,2-triphenylpropane. The purity of the products was demonstrated by vapor phase chromatography and spectroscopic analysis. Attempts to prepare 2,2-diphenylbutane by three procedures utilizing acid-catalyzed condensations led to mixtures of dimeric products. The major saturated component of each of these was proven by spectroscopic analysis to be 1-ethyl-3-phenyl-1,2,3-trimethylindan (VI), rather than 1,3-diethyl-1-methyl-3-phenylindan (VII), as previously proposed. A plausible rationale for the formation of VI is outlined. Methods previously used to prepare 1,2-diphenyl-2-methylpropane were shown to give mixtures containing three other isomers as well. The mechanisms of the carbonium ion processes leading to these isomers are discussed.

Several di- and triphenylbutanes were needed for comparison with possible intermediates in the reactions of butylbenzenes with aluminum chloride.[2] In this paper we report successful synthetic methods applied in the preparation of the pure hydrocarbons, as well as certain interesting aspects of side reactions encountered in syntheses that were unsatisfactory for the preparation of pure hydrocarbons.

The syntheses of 1,1-, 1,2-, and 1,3-diphenylbutane involved the condensation of phenylmagnesium bromide with ethyl *n*-butyrate, of benzylmagnesium chloride with propiophenone, and of the Grignard reagent from β-bromoethylbenzene with acetophenone as previously described.[3] The only modification of the reported procedures was that the intermediate carbinols (1,1-diphenyl-1-butanol, 1,2-diphenyl-2-butanol, and 1,3-diphenyl-3-butanol) were directly hydrogenated in good yields to the corresponding hydrocarbons,[4] rather than dehydrating and reducing the intermediate alkenes.

In the synthesis of 1,1-diphenyl-2-methylpropane, the intermediate carbinol, 1,1-diphenyl-2-methyl-1-propanol, was obtained both by the condensation of isopropylmagnesium chloride with benzophenone[5] and of phenylmagnesium bromide with methyl isobutyrate.[5a,6] The latter method proved to be superior because it gave a much better yield of a cleaner product. Direct catalytic hydrogenation of both 1,1-diphenyl-2-methyl-1-propanol and its dehydration product, 1,1-diphenyl-2-methyl-1-propene, gave good yields of 1,1-diphenyl-2-methylpropane.

The DL- and *meso* forms of 2,3-diphenylbutane were obtained by the coupling of the Grignard reagent of α-bromoethylbenzene as reported.[7,8] The *meso* isomer was also obtained in low yield by treatment of *sec*-butylbenzene with aluminum chloride and *t*-butyl chloride in benzene at room temperature.[2] This latter procedure was based on work of Serres and Fields[9] with cumene and benzene.

The synthesis of 2,2-diphenylbutane was previously reported by the condensation of 2-phenyl-2-butanol with benzene in the presence of aluminum chloride.[3] It was also made by the alkylation of the sodium salt of 1,1-diphenylethane with ethyl bromide in liquid ammonia.[10] The former method was reported to give a very low yield; when the latter method was used, difficulties were experienced in the separation of the product from unaltered 1,1-diphenylethane. Attempts to prepare this compound either by alkylation of benzene with 2-chloro-2-phenylbutane using ferric chloride or aluminum chloride–nitromethane catalysts or by the condensation of benzene with 2-phenyl-2-butene in the presence of concentrated sulfuric acid gave rise only to higher boiling bimolecular condensation products. These bimolecular condensation products were shown to be a mixture of three components in a molar ratio of about 7:1:1. Isolation of the major saturated component in good purity was achieved by preparative vpc; analysis of its infrared, nmr, and mass spectra indicated it to be 1-ethyl-3-phenyl-1,2,3-trimethylindan (VI) and not 1,3-diethyl-1-methyl-3-phenylindan (VII) as assumed previously.[3,11] The former structure is also in better agreement with that of the product expected on the basis of the general mechanism postulated for such bimolecular condensation reactions.[12] The minor saturated component was not isolated in a form pure enough to allow its identification. However, it is probably VII, resulting from the presence of small amounts of α-ethylstyrene in the reaction medium. The other minor component is unsaturated. It is probably 3,4-dimethyl-2,4-diphenyl-2-hexene (V), resulting from loss of a proton from the cation IV instead of the cyclialkylation of this intermediate that yields VI (see Scheme I).

Finally, pure 2,2-diphenylbutane was conveniently obtained in good yields by the reduction of 3,3-diphenyl-2-butanone by a modified Huang-Minlon

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(1) (a) This work was in part abstracted from the Ph.D. Dissertation of A. A. K., The University of Texas, 1964. (b) Robert A. Welch Postdoctoral Fellow, 1964–1965.

(2) R. M. Roberts, A. A. Khalaf, and R. N. Greene, *J. Am. Chem. Soc.*, **86**, 2846 (1964).

(3) K. T. Serijan and P. H. Wise, *ibid.*, **74**, 365 (1952).

(4) R. M. Roberts, G. A. Ropp, and O. K. Neville, *ibid.*, **77**, 1764 (1955).

(5) (a) P. Sabatier and M. Murat, *Compt. Rend.*, **156**, 1430 (1913); (b) *Ann. Chim.* (Paris), **4**, 253 (1915).

(6) W. Schlenk and E. Bergmann, *Ann.*, **463**, 47 (1928); *Chem. Abstr.*, **22**, 4494 (1928).

(7) A. I. Lepin, *J. Russ. Phys. Chem. Soc.*, **44**, 1190 (1912).

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

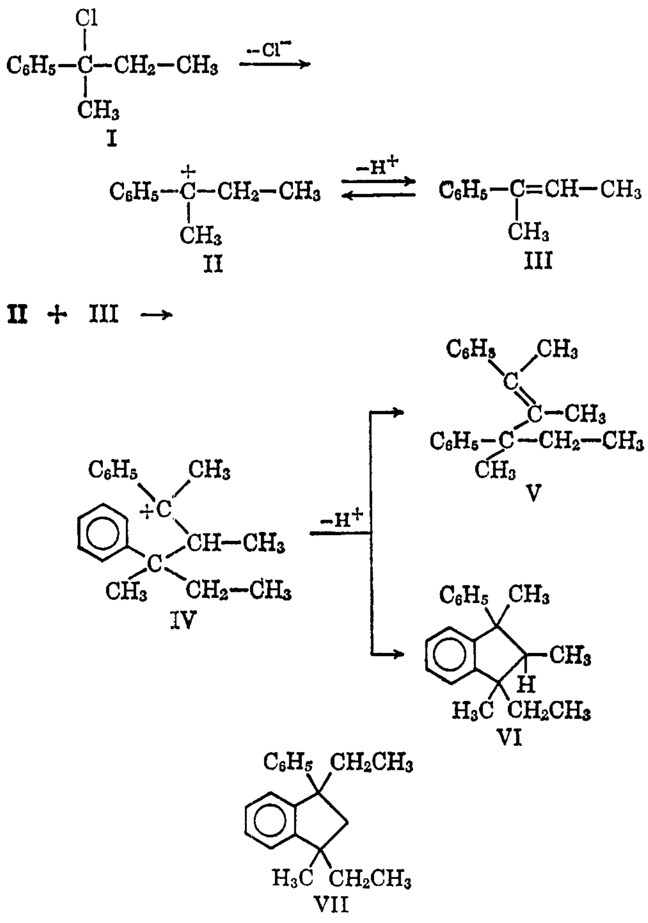
(9) C. Serres and E. K. Fields, *J. Org. Chem.*, **28**, 1624 (1963).

(10) T. Weinstock and S. N. Lewis, *J. Am. Chem. Soc.*, **79**, 6243 (1957).

(11) C. G. Overberger, E. M. Pearce, and D. Tanner, *ibid.*, **80**, 1761 (1958).

(12) L. R. C. Barclay in "Friedel-Crafts and Related Reactions," Vol. II, Part 2, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, pp 944–962, and references there given.

SCHEME I

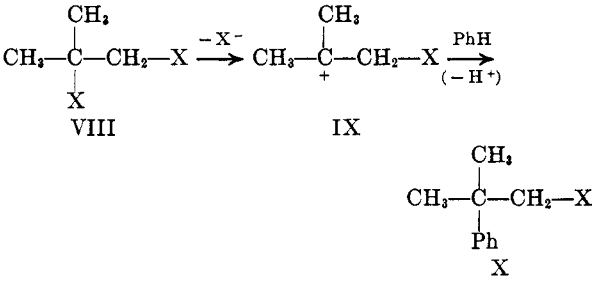


method.[13] This simple modification (see Experimental Section) gives a more satisfactory procedure for the reduction of such hindered ketones. 2-2-Diphenylbutane was also obtained in *ca.* 15% yield by the coupling of phenylmagnesium bromide with 2-phenyl-2-chlorobutane.

The synthesis of 1,2-diphenyl-2-methylpropane (XV) deserves special comment. Somerville and Spoerri[8] reported two methods for making this compound. When these procedures were followed, mixtures were obtained in both cases, consisting of 1,2-diphenyl-2-methylpropane (XV), 1,1-diphenyl-2-methylpropane (XVI), and DL- and *meso*-2,3-diphenylbutane (XXI). Somerville and Spoerri recognized the presence of *meso*-2,3-diphenylbutane in the 1,2-diphenyl-2-methylpropane owing to its crystalline nature and low solubility in the medium; they were apparently unaware of the presence of the other two isomers.

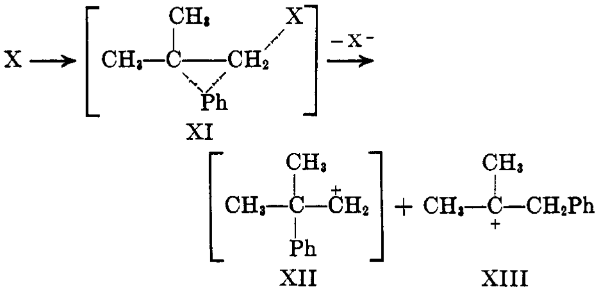
Subsequent attempts were made to obtain pure 1,2-diphenyl-2-methylpropane by reaction of neophyl chloride (X, X = Cl) with benzene using milder catalysts such as ferric chloride and aluminum chloride–nitromethane.[14] With these catalysts, however, an equilibrium mixture of XV and XVI was formed. Both forms of XXI were missing from the product mixtures. This indicated that the formation of XXI is subsequent to alkylation and requires a catalyst strong enough to abstract a hydride ion (see below). This was substantiated by the fact that when pure samples of both XV and XVI were treated with aluminum chloride, they were easily equilibrated, and both forms of XXI were also produced.[2] When ferric chloride or aluminum chloride–nitromethane catalysts were used, the respective diphenylbutanes were recovered unchanged.

To account for the products obtained in the alkylation of benzene with neophyl chloride (X, X = Cl) and isobutylene dibromide (VIII, X = Br) using Friedel–Crafts catalysts, the mechanisms outlined in eq 1–8 are proposed.



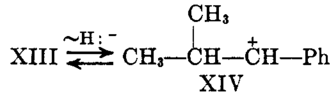
$$CH_3-\overset{CH_3}{\underset{X}{C}}-CH_2-X \xrightarrow{-X^-} CH_3-\overset{CH_3}{\underset{+}{C}}-CH_2-X \xrightarrow[(-H^+)]{PhH} CH_3-\overset{CH_3}{\underset{Ph}{C}}-CH_2-X \quad (1)$$

VIII IX X



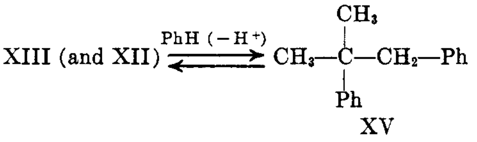
$$X \longrightarrow \left[CH_3-\overset{CH_3}{C}\cdots CH_2\cdots X;\ Ph \text{ bridged}\right] \xrightarrow{-X^-} \left[CH_3-\overset{CH_3}{\underset{Ph}{C}}-\overset{+}{C}H_2\right] + CH_3-\overset{CH_3}{\underset{+}{C}}-CH_2Ph \quad (2)$$

XI XII XIII



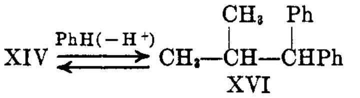
$$XIII \underset{}{\overset{\sim H:^-}{\rightleftarrows}} CH_3-\overset{CH_3}{C}H-\overset{+}{C}H-Ph \quad (3)$$

XIV



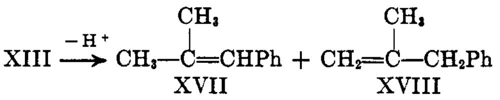
$$XIII\ (\text{and } XII) \overset{PhH\ (-H^+)}{\rightleftarrows} CH_3-\overset{CH_3}{\underset{Ph}{C}}-CH_2-Ph \quad (4)$$

XV



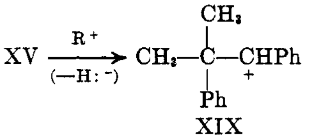
$$XIV \overset{PhH(-H^+)}{\rightleftarrows} CH_3-\overset{CH_3}{C}H-\overset{Ph}{C}HPh \quad (5)$$

XVI



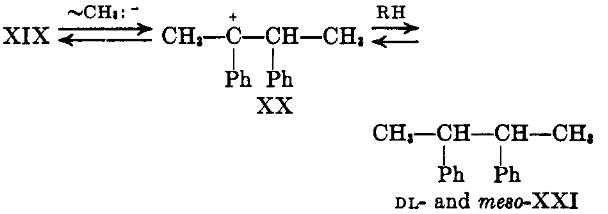
$$XIII \xrightarrow{-H^+} CH_3-\overset{CH_3}{C}=CHPh + CH_2=\overset{CH_3}{C}-CH_2Ph \quad (6)$$

XVII XVIII



$$XV \xrightarrow[(-H:^-)]{R^+} CH_3-\overset{CH_3}{\underset{Ph}{C}}-\overset{+}{C}HPh \quad (7)$$

XIX



$$XIX \overset{\sim CH_3:^-}{\rightleftarrows} CH_3-\underset{Ph}{\overset{+}{C}}-\underset{Ph}{C}H-CH_3 \overset{RH}{\rightleftarrows} CH_3-\underset{Ph}{C}H-\underset{Ph}{C}H-CH_3 \quad (8)$$

XX

DL- and *meso*-XXI

In the case of isobutylene dibromide, the first step is the formation of the tertiary carbonium ion (IX, X = Br), which in turn alkylates benzene to yield neophyl bromide (X, X = Br) (eq 1). This is reasonable because of the comparative inactivity of the bromine atom

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

[14] L. Schmerling and J. P. West, *ibid.*, **76**, 1917 (1954).

attached to the primary carbon atoms.[15] Participation of the phenyl group appears to be essential in the removal of the primary halogen atom from the neophyl halide (eq 2), since alkylation of benzene with neophyl chloride was readily achieved in the presence of the weak catalysts, ferric chloride and aluminum chloride–nitromethane complex, whereas, when the latter catalyst was used,[15] reaction of the primary chlorine of 1,3-dichloro-3-methylbutane was negligible and a 55% yield of 1-chloro-3-methyl-3-phenylbutane was obtained. No diphenylpentane was produced.

The production of an equilibrium mixture of XV and XVI from the reaction of benzene with either neophyl chloride or isobutylene dibromide, even when the weak catalysts were used, suggests that the tertiary carbonium ion XIII is produced as an intermediate in both cases (eq 2)[16a] and equilibration of the tertiary ion XIII with the secondary (benzylic) ion (XIV) by a 1,2 hydride shift (eq 3) occurs rapidly[16b] prior to the second alkylation that leads to the formation of XV and XVI (eq. 4 and 5). The presence of olefins (probably XVII and XVIII, eq 6) among the reaction products was indicated by the observation of an olefinic absorption band in the infrared spectra of the crude mixtures, as well as by the ability of these mixtures to decolorize potassium permanganate and bromine solutions. The rearrangements of XV and XVI to DL- and *meso*-XXI require the strong catalyst aluminum chloride for hydride abstraction steps such as that indicated in eq. 7; a 1,2 methyl shift may then occur, followed by hydride exchange (eq 8).[17]

We finally succeeded in making a pure sample of XV by the coupling of 2-chloro-2-phenylpropane with benzylmagnesium chloride. To our knowledge this furnishes the first method for the preparation of this compound in a pure state.

The previously unreported 2-methyl-1,1,2-triphenylpropane was also desired. Attempted preparation of this compound by the coupling of diphenylmethylmagnesium chloride (prepared as directed by Gilman and Kirby[18]) with 2-chloro-2-phenylpropane was unsuccessful. Only self-coupling was observed. Subsequently, two methods were developed for its synthesis. The first of these involved the condensation of phenylmagnesium bromide with ethyl α-phenylisobutyrate[3] followed by catalytic reduction of the intermediate carbinol.[4] The second method utilized the coupling of the sodium salt of diphenylmethane with 2-chloro-2-phenylpropane in liquid ammonia.[10]

Experimental Section

The organic chemicals used were of reagent grade and were purchased from the usual suppliers. Melting points are uncorrected. Infrared spectra were obtained with a Beckman IR5A spectrometer. The H^1 nmr spectra were recorded on a Varian Associates A-60 spectrometer. Vapor phase chromatographic (vpc) analyses were made on a Beckman GC2A, Wilkens Autoprep, or a Wilkens Hi-Fi instrument. Mass spectra were determined by means of a Consolidated Electrodynamics Corp. spectrometer. The purity and identity of all of the starting materials, as well as the identity of the final products, were determined by vpc and infrared analysis and, in some cases, also by nmr and/or mass spectrometric analysis. In all the syntheses, emphasis was on purity rather than quantity, so that the yields were not optimum in most cases.

Synthesis of 1,1-, 1,2-, and 1,3-Diphenylbutane.—The intermediate carbinols, 1,1-diphenyl-1-butanol, 1,2-diphenyl-2-butanol, and 1,3-diphenyl-3-butanol, were prepared as described by Serijan and Wise.[3] The crude carbinols (shown by vpc and infrared analysis to be at least 95% pure) were reduced to the corresponding hydrocarbons by hydrogen and palladium on carbon in glacial acetic acid containing perchloric acid.[4]

1,1-Diphenylbutane was obtained in 70% over-all yield: bp 116–117° (2 mm), n^{20}_{D} 1.5566.

1,2-Diphenylbutane was obtained in 50% over-all yield: bp 122–123° (2.2 mm), n^{20}_{D} 1.5485. The yield in the hydrogenation step alone was 88%.

1,3-Diphenylbutane was obtained in 62% over-all yield: bp 158–159° (14 mm), n^{20}_{D} 1.5522.

The nmr spectra of the above three diphenylbutanes were consistent with their formulations.

Synthesis of 1,1-Diphenyl-2-methylpropane (XVI). A. From Isopropylmagnesium Chloride and Benzophenone.—The procedure was that used by Sabatier and Murat[5] for the preparation of 1,1-diphenyl-2-methyl-1-propanol. One mole of isopropylmagnesium chloride and 0.9 mole of benzophenone afforded a crude product mixture that was shown by vpc and infrared analysis to be a mixture of unchanged benzophenone and the desired carbinol. Leaving the mixture overnight resulted in the separation of 40 g of benzophenone. The remainder of this mixture was subjected to catalytic reduction[4] without further purification. The reduction product, shown by vpc and infrared analysis to be a mixture of diphenylmethane and 1,1-diphenyl-2-methylpropane, was carefully distilled through a 100-cm nichrome-spiral column using a reflux ratio of 98:2. The following fractions were collected at 29-mm pressure: (a) bp 152–153°, 80 g; (b) bp 154–168°, 29 g; and (c) bp 168–169°, 40 g. Fraction a was shown to be pure diphenylmethane, fraction b, a mixture of diphenylmethane (70%) and 1,1-diphenyl-2-methylpropane (30%), and fraction c, *ca.* 98% pure 1,1-diphenyl-2-methylpropane, n^{25}_{D} 1.5582. Its nmr spectrum was consistent with its formulation.

B. From Phenylmagnesium Bromide and Methyl Isobutyrate.—This procedure was applied previously by Sabatier and Murat[5a] as well as by Schlenk and Bergmann[6] for the preparation of 1,1-diphenyl-2-methyl-1-propanol. The crude carbinol we obtained was shown by vpc and infrared analysis to be almost pure. Direct reduction of this carbinol[4] gave 1,1-diphenyl-2-methylpropane in 75% over-all yield based on methyl isobutyrate. In another experiment the carbinol was dehydrated by refluxing with 20% aqueous sulfuric acid for 3 hr. The resultant olefin was then reduced by hydrogen with palladium on carbon in 95% ethyl alcohol to give 1,1-diphenyl-2-methylpropane in 66% over-all yield based on methyl isobutyrate. Both the physical and the spectroscopic properties of 1,1-diphenyl-2-methylpropane obtained in method B were identical with those of the same compound obtained in method A.

Synthesis of DL- and *meso*-2,3-Diphenylbutane (XXI).—These two isomers were obtained by the Grignard coupling of α-bromoethylbenzene as described in the literature.[7,8] DL-2,3-Diphenylbutane, bp 111–112° (1.8 mm), n^{20}_{D} 1.5555, was obtained in 15% yield. The *meso* isomer, mp 126–127°, was obtained in 24% yield.

Attempted Synthesis of 2,2-Diphenylbutane. A. By Reaction of 2-Chloro-2-phenylbutane and Benzene Using Ferric Chloride Catalyst. Preparation of 2-Phenyl-2-butanol.—This was prepared in 58% yield by the method of Serijan and Wise:[3] bp 96–97° (15 mm), n^{20}_{D} 1.5194.

Preparation of 2-Phenyl-2-chlorobutane.—The procedure given here is a modification of that used by Schoepfle and Ryan[19] for the preparation of methyldiphenylchloromethane. Following

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[15] L. Schmerling, R. W. Welch, and J. P. West [*J. Am. Chem. Soc.*, **78**, 5406 (1956)] gave a similar explanation for isolation of 1-chloro-3-methyl-3-phenylbutane from reaction of 1,3-dichloro-3-methylbutane with benzene.

[16] (a) There is no direct evidence either for or against the existence of the primary ion XII in these reactions. In those catalyzed by ferric chloride or aluminum chloride–nitromethane, however, it is unlikely that XII is produced, since it has been shown that a primary chlorine is unreactive toward alkylation with these catalysts (ref 15 and unpublished data from our laboratories). (b) Addititional support for this part of the mechanism comes from the observation[2] that treatment of isobutylbenzene with *t*-butyl chloride and aluminum chloride in benzene solution produces a 2:1 mixture of XV and XVI, with traces of DL- and *meso*-XXI.

[17] A more detailed discussion of these rearrangements was given in the preceding paper.[2]

[18] H. Gilman and J. E. Kirby, *J. Am. Chem. Soc.*, **48**, 1733 (1926).

[19] C. S. Schoepfle and J. D. Ryan, *ibid.*, **52**, 4021 (1930).

this procedure, the chloride was obtained by bubbling dry hydrogen chloride through an ice-cooled mixture of 69 g (0.457 mole) of 2-phenyl-2-butanol, 80 g (0.72 mole) of dry calcium chloride, and 137 ml of dry benzene. The treatment was continued for 4 hr, after which the solution was filtered into a flask immersed in an ice–salt bath, and dry nitrogen was bubbled into the cold filtrate for 3 hr to remove any dissolved hydrogen chloride. Vpc analysis of this solution indicated only one component, and both vpc and infrared analysis indicated the absence of any unchanged carbinol.

Reaction of 2-Chloro-2-phenylbutane with Benzene and Ferric Chloride.—The above chloride solution, kept at a temperature below 10°, was added over a period of 2 hr to a previously cooled, stirred mixture of 400 g of benzene and 10 g (0.06 mole) of anhydrous ferric chloride. The mixture was stirred at room temperature for another 1.5 hr and decomposed with dilute hydrochloric acid. The organic layer was separated, washed with 10% sodium bicarbonate and water, then dried over anhydrous calcium chloride. The solvent was distilled at atmospheric pressure and the residue was distilled under vacuum to give 47 g of a volatile product, bp 147° (3 mm), $n^{25}_{\rm D}$ 1.5645. This was shown by vpc analysis to be a mixture of three components that constituted 12, 11, and 77%, in order of increasing vpc retention time on a Carbowax 20 M column, respectively. Infrared analysis of this mixture revealed the presence of an olefinic absorption band at 1690 cm^{-1}.

B. By Reaction of 2-Chloro-2-phenylbutane and Benzene Using Aluminum Chloride–Nitromethane Complex Catalyst.—A benzene solution of 2-chloro-2-phenylbutane was prepared from 4 g of 2-phenyl-2-butanol as previously described. This was added to a stirred, hydrogen chloride saturated solution of 0.1 g of aluminum chloride and 0.15 ml of nitromethane in 50 ml of benzene at 0° as directed for the alkylation of toluene by 2-chloro-2-(*p*-tolyl)propane.[20] This gave 2.82 g of solvent-free product which was shown by vpc and infrared analysis to consist of the same three components obtained in A, with a composition of 6, 5, and 89%, respectively.

C. By Reaction of 2-Phenyl-2-butene with Benzene and Concentrated Sulfuric Acid Catalyst. Preparation of 2-Phenyl-2-butene.—2-Phenyl-2-butanol was dehydrated by the action of heat and a trace of iodine.[21] Water was distilled at atmospheric pressure and the remaining liquid was distilled under vacuum to give 88% yield of product, bp 60–65° (4 mm), $n^{25}_{\rm D}$ 1.5303. This product was shown by vpc, infrared, and nmr analysis to be a mixture of *cis*-2-phenyl-2-butene (64%), *trans*-2-phenyl-2-butene (27%), and 2-phenyl-1-butene (9%).[22] Reduction of this alkene mixture by hydrogen and palladium on carbon in 95% ethyl alcohol gave *sec*-butylbenzene as the sole product. The latter was identified by vpc and infrared analysis.

Reaction of the Above Phenylbutene Mixture with Benzene and Sulfuric Acid.—The procedure of Weinstock and Lewis[10] for the preparation of diphenylethane from styrene and benzene was used. Starting with 91 g of the alkene mixture, 85 ml of concentrated sulfuric acid and a total of 550 ml of benzene gave 74 g of a volatile product, bp 145–148° (3 mm), $n^{25}_{\rm D}$ 1.5585. This volatile product was shown by vpc and infrared analysis to be a mixture of the same components obtained before by the reaction of 2-chloro-2-phenylbutane and benzene in the presence of either ferric chloride or aluminum chloride–nitromethane catalysts. In this case these components composed 20, 12, and 68% of the mixture, respectively.

Identification of the Major Product from Reactions A, B, and C.—The distillation fraction from the reaction of 2-chloro-2-phenylbutane with benzene and ferric chloride was shaken with ethyl alcohol at room temperature several times. The major component was then isolated from the alcohol-washed layer in a fairly pure state using a Beckman GC-2A gas chromatograph equipped with a 6 ft × 0.25 in. column packed with Carbowax 20M (30%) on Ultraport and a Beckman fraction collector. This major component, with $n^{25}_{\rm D}$ 1.5624, was shown to have an infrared spectrum in the region 5–6 μ identical with that of the model compound, 1-phenyl-1,3,3-trimethylindan.[23] The nmr spectrum of this compound showed a triplet centered at τ 9.20 (J = 7.0 cps) and an overlapping doublet centered at τ 9.10 (J = 7.2 cps). The combined area of the triplet and the doublet corresponded to six protons; these were identified with the methyl hydrogens of the 1-ethyl group and the 2-methyl group, respectively. It also showed a singlet at τ 8.84 (three protons), a singlet at τ 8.53 (three protons), an apparent quartet centered at τ 8.30 (two protons, J = 7.0 cps), a quartet centered at τ 7.75 (one proton, J = 7.2 cps), and a multiplet centered at τ 2.9 (nine protons). These were assigned to the hydrogens of the 1-methyl group, 3-methyl group, the methylene of the 1-ethyl group, 2-methinyl, and to the aromatic hydrogens, respectively. The mass spectrum of this compound was also consistent with its formulation.

Synthesis of 2,2-Diphenylbutane by Reduction of 3,3-Diphenyl-2-butanone. Preparation of 3,3-Diphenyl-2-butanone.—2,3-Diphenyl-2,3-butanediol was prepared both by the bimolecular reduction of acetophenone[24] and by the reaction of phenylmagnesium bromide with 2,3-butanedione.[25] This diol was converted to 3,3-diphenyl-2-butanone by refluxing with 62% sulfuric acid.[10] The over-all yield of the ketone, bp 175–177° (16 mm), $n^{25}_{\rm D}$ 1.5820, was 42%, based on acetophenone, and 50%, based on 2,3-butanedione, respectively.

Reduction of the Above Ketone by a Modified Huang-Minlon Procedure.—In a typical experiment, 44.8 g (0.2 mole) of the ketone, 260 ml of diethylene glycol, and 60 ml of 85% hydrazine hydrate were introduced into a 500-ml round-bottomed flask equipped with an efficient reflux condenser. Using a direct flame, the above mixture was refluxed for 2 hr. The apparatus was then adapted for simple distillation and the temperature was raised till it reached 190°. The mixture was allowed to cool to room temperature and 40 g (0.71 mole) of potassium hydroxide pellets was added cautiously. After all of the hydroxide was added, the mixture was heated mildly at first, then to reflux temperature for 2 hr. The cold reaction mixture was diluted with water, extracted with Skellysolve B, and dried over anhydrous calcium chloride. The solvent was removed and the residue was distilled to give 35 g (83% yield) of pure 2,2-diphenylbutane, bp 160–162° (19 mm), $n^{25}_{\rm D}$ 1.5648. Its physical and spectroscopic properties were identical in all respects with those of a pure sample of the same compound obtained by the coupling of the sodium salt of 1,1-diphenylethane with ethyl bromide in liquid ammonia as directed by Weinstock and Lewis.[10] The nmr spectrum of 2,2-diphenylbutane was consistent with its formulation.

Synthesis of 2,2-Diphenylbutane by the Coupling of Phenylmagnesium Bromide with 2-Chloro-2-phenylbutane.—Phenylmagnesium bromide was prepared from 15.7 g (0.1 mole) of phenyl bromide and 2.4 g (0.1 g-atom) of magnesium turnings in dry ether. After the reaction was complete, a solution of 16.8 g (0.1 mole) of 2-chloro-2-phenylbutane[22b] in 50 ml of dry ether was added to the stirred mixture. The reaction was slightly exothermic and, after the addition of all the chloride, the reaction mixture was stirred at room temperature overnight. The reaction mixture was cooled and decomposed with ice-cold 10% hydrochloric acid solution. The ether layer was separated, washed several times with water, and dried, and the ether was evaporated. Analysis of the residual liquid by vpc showed that the volatile portion contained *ca.* 15% of 2,2-diphenylbutane and *ca.* 85% of other products.

Reaction of Neophyl Chloride with Benzene and Aluminum Chloride.—Neophyl chloride prepared by two methods[26,27] was pure and had an nmr spectrum consistent with its structure. The alkylation procedure described by Somerville and Spoerri[8] was followed exactly. Alcohol-washed *meso*-2,3-diphenylbutane was separated in 11.6% yield. Distillation of the liquid portion gave a main fraction, bp 159–162° (32 mm), shown by vpc, nmr, and infrared analysis to be a mixture of 1,2-diphenyl-2-methylpropane (62%), 1,1-diphenyl-2-methylpropane (30%),

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(21) A. S. Brown and M. G. Voronkov, *J. Gen. Chem. USSR*, **17**, 1162 (1947); *Chem. Abstr.*, **42**, 1591*b* (1948).

(22) (a) D. J. Cram [*J. Am. Chem. Soc.*, **74**, 2137 (1952)] gave the infrared spectra of these three 2-phenylbutene isomers. (b) D. J. Cram and M. R. V. Sahyun [*ibid.*, **85**, 1257 (1963)] gave the vpc retention times of the same olefins.

(23) This substituted indan was obtained and characterized in this laboratory by Dr. R. N. Greene in a similar reaction of α-methylstyrene with excess benzene in the presence of concentrated sulfuric acid.

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(25) J. Wegmann and H. Dahn, *Helv. Chim. Acta*, **29**, 101 (1946).

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(27) M. S. Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, **61**, 2142 (1939).

and DL-2,3-diphenylbutane (8%). The total yield of these liquid isomers was 52%.

Reaction of Neophyl Chloride with Benzene and Aluminum Chloride–Nitromethane Catalyst.—Neophyl chloride (4.2 g, 0.025 mole) was added over a period of 2 hr to an ice-cooled, stirred solution of 0.67 g (0.05 mole) of aluminum chloride and 1.5 g (0.024 mole) of nitromethane in 20.4 g of benzene. After the addition, the mixture was stirred at room temperature for 1.5 hr. The crude product obtained as usual weighed 4.4 g (83%) and was shown by vpc and infrared analysis to consist of 1,2-diphenyl-2-methylpropane (63%) and 1,1-diphenyl-2-methylpropane (37%).

Reaction of Neophyl Chloride with Benzene and Ferric Chloride.—The procedure described in the previous experiment was used. The reactants were 4.2 g (0.025 mole) of neophyl chloride, 20.4 g (0.256 mole) of benzene, and 0.5 g (0.003 mole) of anhydrous ferric chloride. The product was obtained in 78% yield and was shown by vpc and infrared analysis to consist of 1,2-diphenyl-2-methylpropane (67%) and 1,1-diphenyl-2-methylpropane (33%).

Preparation of Isobutylene Dibromide.—This compound was prepared according to the procedure of Somerville and Spoerri.[8] The dibromide (bp 143–146°, n^{20}_{D} 1.5069) was obtained in 57% yield.

Reaction of Isobutylene Dibromide with Benzene and Aluminum Chloride Catalyst.—The method of Somerville and Spoerri[8] was used. This gave a 9% yield of alcohol-washed *meso*-2,3-diphenylbutane and 50% yield of a liquid product, bp 144–147° (12.8 mm), n^{24}_{D} 1.5565. This liquid product was shown by vpc, infrared, and nmr analysis to consist of 1,2-diphenyl-2-methylpropane (61%), 1,1-diphenyl-2-methylpropane (33%), and DL-2,3-diphenylbutane (6%). A forerun fraction [bp 52–144° (12.8 mm) and 174–184° (atmospheric pressure), n^{24}_{D} 1.5095] was also obtained. This was shown by vpc, infrared, and nmr analysis as well as by qualitative chemical tests to be a mixture of isobutylbenzene[8] (16%) and an unidentified aliphatic bromide (84%).

Preparation of 2-Chloro-2-phenylpropane.—2-Phenyl-2-propanol was prepared by the action of phenylmagnesium bromide on acetone,[3] followed by replacement of the hydroxyl by chlorine by treating the carbinol with dry hydrogen chloride for 2 hr at 0°.[28] The chloride was washed several times with ice-cold water followed by ice-cold 10% sodium bicarbonate solution and finally by ice-cold water. It was then dried over anhydrous calcium chloride and stored in a refrigerator. The over-all yield of the chloride (shown by vpc and infrared analysis to be at least 95% pure) was 84%, based on phenylmagnesium bromide. This chloride was used in the next step without any further purification.

Synthesis of 1,2-Diphenyl-2-methylpropane (XV).—In a typical synthesis, benzylmagnesium chloride was prepared from 4.8 g (0.20 g-atom) of magnesium, a small crystal of iodine, 25.3 g (0.20 mole) of benzyl chloride, and a total of 120 ml of dry ether. To the resulting Grignard reagent was added with cooling a solution of 27.5 g (0.18 mole) of 2-chloro-2-phenylpropane in an equal volume of dry ether at such a rate that gentle refluxing took place. When all of the chloride was added, stirring was continued overnight at room temperature and for an additional 1 hr at reflux temperature. The reaction mixture was cooled and decomposed with ice-cold 15% sulfuric acid solution. The ether layer was separated and the aqueous layer was extracted with 50 ml of ether. The combined ether layer was washed several times with water until neutral to litmus paper and finally dried over anhydrous sodium sulfate. The ether was removed and the residue was distilled twice through a 100-cm nichrome-spiral column using a reflux ratio of 99:1 to give 17 g (45%) of 98% pure 1,2-diphenyl-2-methylpropane, bp 144–145° (9 mm), 148–150° (11 mm), n^{25}_{D} 1.5577. Its vpc retention time on various columns was identical with that of the major component in the products of reaction of neophyl chloride and isobutylene dibromide with benzene and Friedel–Craft catalysts.

The nmr spectrum of this compound showed the following absorptions: a singlet at τ 8.78 (six protons), a singlet at τ 7.25 (two protons), and a multiplet centered at τ 3 (ten protons). These were assigned to the methyl protons, the methylene protons, and the aromatic protons, respectively. Identical absorptions were also shown (among others) in the nmr spectra of the mixtures previously obtained. The mass spectrum of pure 1,2-diphenyl-2-methylpropane was also consistent with its structure.

Treatment of 1,2-Diphenyl-2-methylpropane and 1,1-Diphenyl-2-methylpropane with Aluminum Chloride–Nitromethane and Ferric Chloride Catalysts.—The reactants were mixed in the proportions, diphenylbutane (1 mole), benzene (10 moles), aluminum chloride (0.1 mole) in nitromethane (2.78 mole) or ferric chloride (0.16 mole), and stirred magnetically for 4–24 hr. The reaction mixture was decomposed with water, washed with 10% sodium bicarbonate solution and water, and dried, and benzene was distilled at atmospheric pressure. The residue was chilled to −5° (to separate any *meso*-2,3-diphenylbutane that might have been formed) and then analyzed by vpc and infrared. In all cases the starting materials were found to be unchanged.

Synthesis of 2-Methyl-1,1,2-triphenylpropane. A. By the Alkylation of Diphenylmethane with 2-Chloro-2-phenylpropane in Liquid Ammonia.—The procedure used was essentially the one used by Weinstock and Lewis[10] for the preparation of 2,2-diphenylbutane by the reaction of the sodium salt of diphenylethane with ethyl bromide. 2-Methyl-1,1,3-triphenylpropane, bp 192–193° (5 mm), mp 49–50°, was obtained in 76% yield. It was pure according to vpc analysis, and its infrared and mass spectra were consistent with its formulation. Its nmr spectrum exhibited the following absorptions: a singlet at τ 8.60 (six protons), a singlet at τ 5.87 (one proton), and a multiplet centered at τ 2.93 (15 protons). These were assigned to the methyl protons, the methinyl proton, and the aromatic protons, respectively.

Anal. Calcd for $C_{22}H_{22}$: C, 92.30; H, 7.69. Found: C, 91.83; H, 7.63.

B. By Reaction of Ethyl α-Phenylisobutyrate with Phenylmagnesium Bromide Followed by Catalytic Reduction.—α,α-Dimethylbenzyl cyanide was prepared as described by Cope, Foster, and Towle.[29] It was converted to ethyl α-phenylisobutyrate (bp 236–237°, n^{25}_{D} 1.4906) by essentially the same procedure used for the alcoholysis of benzyl cyanide.[30] The ester, dissolved in an equal volume of dry ether, was added to about 3 molar equiv of phenylmagnesium bromide prepared as usual in dry ether. The reaction mixture was stirred at room temperature for 24 hr, refluxed for 2 hr, and decomposed with saturated ammonium chloride solution, the ether layer was dried, and the ether was evaporated. The crude residue was hydrogenated.[4] Distillation of the hydrogenated mixture gave 2-methyl-1,1,2-triphenylpropane in 53% yield. This was shown to have identical physical and spectroscopic properties with those of the same compound obtained in method A.

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