Registry No.—2-Benzylbenzoin, 7540-93-4; 5-benzyl-5-hydroxy-4-decanone, 26431-42-5; *cis*-α,α'-stilbenediol diacetate, 26431-43-6; benzyl *n*-butyl ketone, 25870-62-6; Li[PhCOFe(CO)$_4$], 26402-46-0; Li[*p*-$CH_3C_6H_4COFe(CO)_4$], 26402-47-1; Li[*n*-$C_4H_9COFe(CO)_4$], 26402-48-2; $C_6H_5CH_2Br$, 100-39-0; $C_6H_5CH_2I$, 620-05-3; C_6H_5COCl, 98-88-4; CH_3COCl, 75-36-5; $C_6H_5CH{=}CHCOCl$, 102-92-1; Li[$PhCONi(CO)_3$], 26402-49-3; Li[*p*-$CH_3C_6H_4CONi(CO)_3$], 26402-50-6; Li[*n*-$C_4H_6CONi(CO)_3$], 26402-51-7; $C_6H_5CH_2Cl$, 100-44-7.

Synthesis of Long-Chain *tert*-Alkylbenzenes by the Grignard–Wurtz Reaction

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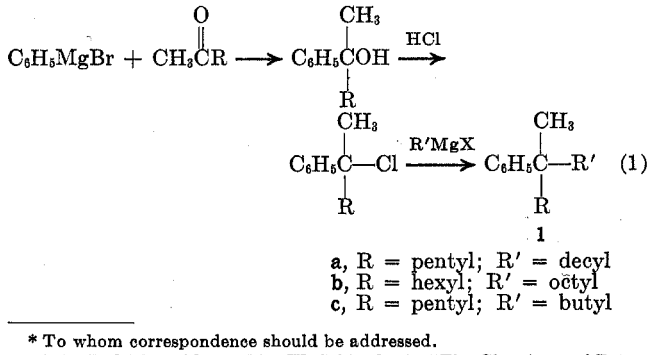
The Grignard–Wurtz reaction was extended to the synthesis of eleven long-chain mono- and di-*tert*-alkylbenzenes. In this reaction nonpolar media, such as *n*-hexane or *n*-heptane, gave yields double those obtained in diethyl ether. In nonpolar media the major side reaction was substitution of halogen by hydrogen in the starting benzylic halides. This reduction apparently does not proceed by functional exchange.

The synthesis of high-molecular-weight hydrocarbons of good purity is of continuing interest for the elucidation of structure–property relationships.[1] In our own laboratories we were interested in *tert*-alkylbenzenes, particularly di-*tert*-alkylbenzenes. Only 25 mono-*tert*-alkylbenzenes have been prepared[2] by routes not likely to lead to rearranged side chains and in none of these did the *tert*-alkyl group have more than 12 carbon atoms. We could find no example, other than *p*-di-*tert*-butylbenzene, of a di-*tert*-alkylbenzene of unquestionable structure. In this paper we report 11 new *tert*-alkylbenzenes, four of which have a *p*-di-*tert*-alkyl structure.

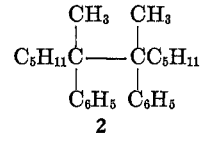
Two general routes to *tert*-alkylbenzenes have been described in the literature: an eight-step sequence developed by Rabjohn involving as the key step the 1,4 addition of Grignard reagents to alkylidenecyanoacetates,[2j,3] and the Grignard–Wurtz reaction.[2a,c,k]

In contrast to the alkylidenecyanoacetate route, the Grignard–Wurtz route involves only three steps: preparation of a tertiary alcohol by the familiar Grignard–ketone condensation, conversion of the alcohol to a tertiary chloride by means of anhydrous hydrogen chloride, and coupling of the tertiary chloride with a second Grignard reagent. Because of its apparent simplicity, this route seemed more suitable for extension to the synthesis of long-chain *tert*-alkylbenzenes and especially di-*tert*-alkylbenzenes.



a, R = pentyl; R′ = decyl
b, R = hexyl; R′ = octyl
c, R = pentyl; R′ = butyl

We first investigated this scheme for the synthesis of 6-methyl-6-phenylhexadecane (**1a**) by the coupling of decylmagnesium bromide with 2-chloro-2-phenylheptane. This reaction yielded 1-decane, 1-decene, 2-phenylheptane, a mixture of isomeric 2-phenylheptenes, eicosane, and a high-boiling solid residue in addition to the desired **1a**. The high-boiling solid residue consisted predominantly of 6,7-dimethyl-6,7-diphenyldodecane (**2**), a dimeric coupling product derived from 2-chloro-2-phenylheptane.[4] No chlorodecane and only



2

small amounts, <2%, of 1-bromodecane could be detected in the product mixture by gas chromatography.

The product distribution, shown in Table I, was strongly influenced by changes in the reaction medium. Thus, the amount of **1a** in the product mixture, expressed as gas chromatography area %, increased from 7.5% in tetrahydrofuran at 60–80°, to 22% in refluxing ether, to 46% in *n*-hexane at 70–75°. The concentration of 2-phenylheptane remained relatively constant at 14–16% of the product mixture. On the other hand, polar media favored the formation of 1-decene, decane, and 2-phenyl-2(1)-heptene.[5]

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(2) (a) A. D. Petrov and E. P. Zakharov, *J. Gen. Chem. USSR*, **27**, 3019 (1957); (b) A. D. Petrov, G. I. Nikishin, and V. D. Vorobiev, *ibid.*, **28**, 1809 (1958); (c) M. S. Malinovskii and A. A. Yavorovskii, *ibid.*, **25**, 2169 (1955); (d) A. D. Petrov, G. I. Nikishin, and V. D. Vorobiev, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 717 (1960); (e) A. D. Petrov, O. M. Nefedov, and Yu. N. Ogibin, *ibid.*, 1004 (1957); (f) K. Ziegler, H. Grimm, and R. Willer, *Justus Liebigs Ann. Chem.*, **542**, 90 (1940); (g) V. N. Gramenitskaya, G. I. Nikishin, and A. D. Petrov, *Dokl. Akad. Nauk SSSR*, **128**, 548 (1959); (h) M. S. Malinovskii and A. A. Yavorovskii, *Ukr. Khim. Zh.*, **21**, 723 (1955); *Chem. Abstr.*, **50**, 11961 (1956); (i) G. M. K. Hughes, *J. Chem. Soc.*, 3703 (1958); (j) E. R. Lynch and E. B. McCall, *ibid.*, 1254 (1960); (k) M. Inatome, J. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Amer. Chem. Soc.*, **74**, 292 (1952); (l) F. W. Gray and K. J. Krems, *J. Org. Chem.*, **26**, 209 (1961); (m) L. V. Bugrova and I. P. Tsukervanik, *Zh. Org. Khim.*, **1**, 714 (1965); (n) H. S. Block, U. S. Patent 3,268,610 (1966).

(3) (a) N. Rabjohn, L. V. Phillips, and R. J. DeFeo, *J. Org. Chem.*, **24**, 1964 (1959); (b) G. Desgrandchamps, A. Deluzarche, and A. Maillard, *Bull. Soc. Chim. Fr.*, 264 (1961).

(4) The structure of this product was assigned on the basis of elemental and nmr analyses and its facile thermal cleavage to a 1:1 mixture of 2-phenylheptane and 2-phenyl-2(1)-heptene.

(5) Under the conditions of gas chromatographic analysis, compound **2** which was also formed in the reaction underwent partial cleavage to give an equimolar mixture of 2-phenylheptane and 2-phenyl-2(1)-heptene. Therefore, the amounts of 2-phenylheptane and 2-phenyl-2(1)-heptene shown in Table I are the sums of the amounts produced directly as well as by the cleavage reaction.

TABLE I

EFFECT OF SOLVENT ON PRODUCT DISTRIBUTION IN THE REACTION OF DECYLMAGNESIUM BROMIDE WITH 2-CHLORO-2-PHENYLHEPTANE

	Products, area %					
Solvent	1-Decene	Decane	2-Phenyl-heptane	2-Phenyl-2(1)-heptene	Eicosane	6-Methyl-6-phenyl-hexadecane
Hexane, 70–75°	7.5	19.4	16.5	4.3	4.6	46.7
Ethyl ether, 35–40°	20.8	25.1	15.1	10.0	...[a]	22.4
THF, 60–80°	28.9	30.6	13.8	13.7	2.5	7.5

[a] Undetermined.

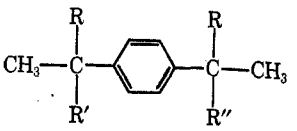
TABLE II

MONO-*tert*-ALKYLBENZENES

				Calcd, %			Found, %		
Compd	Bp, °C (mm)	$n^{25}D$	Yield, %	C	H	Mol wt	C	H	Mol wt
1a	209 (10)	1.4838	30	87.26	12.74	316.6	87.16	12.41	316
1b	205 (10)	1.4838	32	87.34	12.66	302.5	87.25	12.49	302
1c	146 (10)	1.4883	17	87.87	12.13	232.4	87.78	12.11	232

TABLE III

DI-*tert*-ALKYLBENZENES AND *tert*-ALKYLPHENYLALKANES



						Calcd, %			Found, %		
R	R′	R″	Bp, °C (mm)	$n^{25}D$	Yield, %	C	H	Mol wt	C	H	Mol wt
Butyl	Butyl	Butyl	135–136 (0.1)	1.4877	11[a]	87.06	12.94	358.7	86.97	12.78	358
Butyl	Hexyl	Hexyl	174 (0.12)	1.4843	16[b]	86.88	13.12	414.8	87.04	12.98	414
Butyl	Octyl	Octyl	194 (0.1)	1.4837	11[c]	86.73	13.27	470.9	86.73	13.31	470
Hexyl	Octyl	Octyl	215 (0.1)	1.4818	11[d]	86.61	13.39	527.0	86.69	13.11	526
Butyl	Butyl	H	109 (0.08)	1.4866	29[e]	87.34	12.66	302.5	87.55	12.68	302
Butyl	Hexyl	H	130 (0.1)	1.4850	22[f]	87.21	12.79	330.6	86.98	12.90	330
Butyl	Octyl	H	145 (0.1)	1.4841	21[g]	87.06	12.94	358.7	87.01	13.06	358
Hexyl	Octyl	H	178 (0.1)	1.4820	21[h]	86.88	13.12	414.8	86.85	13.39	414

Registry numbers: [a] 26279-06-1, [b] 26279-07-2, [c] 26279-08-3, [d] 26279-09-4, [e] 26279-10-7, [f] 26279-11-8, [g] 26322-49-9, [h] 26279-12-9.

The study with 2-chloro-2-phenylheptane and decylmagnesium bromide demonstrated the advantage of conducting the Grignard–Wurtz reaction in nonpolar media such as *n*-hexane or *n*-heptane, an observation which has been made previously.[2a,c,6] We used this technique to prepare the new mono-*tert*-alkylbenzenes shown in Table II. Extension of the reaction to difunctional benzylic chlorides, derived from *p*-diacetylbenzene, afforded the new di-*tert*-alkylbenzenes shown in Table III. The yields of the alkylbenzenes shown in Tables II and III are those of the analytically and chromatographically pure samples having the properties shown; the yields of crude product (70–80% purity) were usually 20–40%. Compound **1a** also was synthesized by the longer Rabjohn sequence[3a] with an overall yield of 23%. Thus, in this case the Grignard–Wurtz procedure proved to be superior in both yield and convenience.

The major side reaction in all of the reactions carried out in hydrocarbon media was reduction of the benzylic chloride to give a secondary alkyl grouping. In the case of the difunctional benzylic halides, the major byproducts were *p*-(*tert*-alkyl)phenylalkanes and -alkenes obtained by Grignard–Wurtz coupling at one reactive site and either reduction or removal of the elements of hydrogen chloride at the other. These mixtures were not separated but were hydrogenated directly to give good yields of the novel *p*-(*tert*-alkyl)phenylalkanes shown in Table III (R″ = H).

In general, the formation of the products observed in these reactions can be accommodated by the radical mechanism proposed by Morrison and coworkers for the reactions of Grignard reagents with the simpler benzyl and α-phenylethyl halides.[7] In the case of the benzyl halides, reduction of the halide was found to proceed by functional exchange between the halide and Grignard reagent.[7b,c] In our own work, carbonation of the reaction mixture resulting from 2-chloro-2-phenylheptane and butylmagnesium bromide gave none of the 2-methyl-2-phenylheptanoic acid to be expected had functional exchange occurred. This result, together with the observation that no chlorodecane was detectable in the reaction of decylmagnesium bromide and 2-chloro-2-phenylheptane, suggests that reduction of α,α-dialkylbenzyl halides occurs by way of disproportionation, cross-disproportionation, or hydrogen abstraction from solvent rather than by functional exchange.[8]

(6) A. D. Petrov, E. P. Zakharov, and L. L. Krasnova, *J. Gen. Chem. USSR*, **29**, 49 (1959).

(7) R. T. Morrison, T. Axenrod, F. L. Bach, Jr., N. P. Loire, C. E. Lorenz, and C. D. Mukai, unpublished results. See (a) T. Axenrod, Ph.D. Thesis, New York University, 1961; *Diss. Abstr.*, **22**, 3848 (1962); (b) F. L. Bach, Jr., Ph.D. Thesis, New York University, 1963; *ibid.*, **24**, 3093 (1964); (c) N. P. Loire, Ph.D. Thesis, New York University, 1960; *ibid.*, **21**, 56 (1960); (d) C. E. Lorenz, Ph.D. Thesis, New York University, 1957; *ibid.*, **18**, 400 (1958); (e) C. D. Mukai, Ph.D. Thesis, New York University, 1955; *ibid.*, **18**, 793 (1958).

(8) Similarly, no functional exchange was observed in reactions of Grignard reagents with α-phenylethyl halides.[7d]

The present work, as well as that of others,[2a,c,5] shows clearly that nonpolar media favor the formation of alkylation products in these reactions. We think it likely that alkylation is favored in nonpolar media because reaction is constrained to take place within unsolvated complexes or aggregates of complexes in a concerted fashion with little opportunity for ions or radicals to diffuse out of the complex cage.[9]

Experimental Section[10]

Materials.—All materials were of the highest quality commercially obtainable. Liquid materials were checked for purity by gas chromatography and redistilled if necessary to bring them to ⩾97 area % purity. *p*-Diacetylbenzene, mp 108–112°, was obtained from Aldrich Chemical Company; the dark color could not be removed by recrystallization from ether, benzene, or acetone; however, gas chromatography indicated less than 2 area % impurity.

2-Phenyl-2(1)-heptene.—2-Phenyl-2-heptanol,[11] 718.3 g (3.74 mol), was distilled over a trace of potassium hydrogen sulfate to obtain 435.7 g of material, bp 100–115° (10 mm), n^{25}D 1.5108–1.5242, and 226.4 g (1.18 mol) of recovered alcohol. The yield of olefin, based on recovered alcohol, was 98%. Gas chromatographic examination of the product indicated the presence of three substances, two of which were incompletely resolved. The ratio of the area of the two unresolved peaks to that of the third peak was 10:1. The gas chromatographic analysis is consistent with a mixture of *cis*- and *trans*-2-phenyl-2-heptene and 2-phenyl-1-heptene. A strong peak at 908 cm^{-1} in the infrared spectrum was indicative of the C=CH$_2$ grouping.

Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.56; H, 10.42.

1,4-Bis(1-hydroxy-1-methylheptyl)benzene.—To a solution of 7.75 mol of hexylmagnesium bromide in 1050 ml of ether, maintained at reflux, was added in small portions a total of 500 g (3.1 mol) of powdered *p*-diacetylbenzene. The mixture was stirred vigorously at reflux for an additional 4 hr, and then at room temperature for 2 days. The mixture was hydrolyzed with ammonium chloride and worked up in the conventional manner. The solid product obtained upon concentration of the solvent was recrystallized from hexane to obtain 219.1 g of 1,4-bis(1-hydroxy-1-methylheptyl)benzene, mp 109–112°.

The filtrate and hexane mother liquors were combined and distilled over 0.5 g of potassium carbonate to give an additional 296.1 g of material, bp 185–190° (0.65 mm). The crude 1,4-bis(1-hydroxy-1-methylheptyl)benzene so obtained was recrystallized from hexane to give 213.1 g of material, mp 68–72°; analytical sample, mp 70–73°. A total of 432.2 g (42%) of the diol was obtained. Infrared spectra of the two crystalline modifications, presumably the meso compound and a *dl* pair, were identical; prominent peaks were noted at 3400 (–OH), 1325 and 1130 (*tert*-OH), 1020 (para-substituted benzene), and 830 and 840 cm^{-1} (doublet, para-substituted benzene).

Anal. Calcd for $C_{22}H_{38}O_2$: C, 78.99; H, 11.45. Found: C, 78.89; H, 11.60.

1,4-Bis(1-hydroxy-1-methylpentyl)benzene.—The reaction of butylmagnesium bromide with *p*-diacetylbenzene was carried out in the manner described above for the reaction of hexylmagnesium bromide and *p*-diacetylbenzene. Solid diol was recovered from the solvent-free product mixture and recrystallized from hexane to obtain 390.7 g (23%) of material, mp 123–128°; analytical sample, mp 127–128°.

Anal. Calcd for $C_{18}H_{30}O_2$: C, 77.66; H, 10.85. Found: C, 77.54; H, 10.94.

3-Methyl-3-phenyloctanenitrile.—Reaction of phenylmagnesium bromide with ethyl 1-methylhexylidenecyanoacetate[12] in the presence of cuprous iodide in the manner described by Rabjohn, *et al.*,[3a] afforded 67% of ethyl 2-cyano-3-methyl-3-phenyloctanoate: bp 125–135° dec (0.20 mm); n^{25}D 1.4980–1.5013; ir 2260 (–CN), 1760 (ester C=O), 2000–1750 (monosubstituted aromatic) and 1250–1030 cm^{-1} (ester COC).

Hydrolysis[3a] and decarboxylation[3a] of the above product over copper powder gave 55% of 3-methyl-3-phenyloctanenitrile: bp 164.0–165.5° (9 mm); n^{25}D 1.5042; ir 2260 (–CN), 766 and 697 cm^{-1} (monosubstituted aromatic).

Anal. Calcd for $C_{15}H_{21}N$: C, 83.66; H, 9.83; N, 6.51. Found: C, 83.28; H, 9.89; N, 6.58.

6-Methyl-6-phenyl-8-hexadecanone.—The reaction of *n*-octylmagnesium bromide with 3-methyl-3-phenyloctanenitrile, carried out in refluxing ether for 18 hr, followed by hydrolysis of the intermediate product, as described by Rabjohn, *et al.*,[3a] afforded 83% of 3-methyl-3-phenyl-8-hexadecanone: bp 137° (0.08 mm); n^{25}D 1.4880; ir 1715 cm^{-1} (C=O).

Anal. Calcd for $C_{23}H_{38}O$: C, 83.57; H, 11.59. Found: C, 83.55; H, 11.24.

6-Methyl-6-phenyl-8-hexadecanol.—Lithium aluminum hydride reduction of 6-methyl-6-phenyl-8-hexadecanone afforded 94% of 6-methyl-6-phenyl-8-hexadecanol: bp 166° (0.30 mm); n^{25}D 1.4910.

Anal. Calcd for $C_{23}H_{40}O$: C, 83.07; H, 12.12. Found: C, 83.23; H, 12.33.

6-Methyl-6-phenyl-7(8)-hexadecene.—6-Methyl-6-phenyl-8-hexadecanol, 320 g (0.96 mol), and 40 g of anhydrous potassium hydrogen sulfate were heated together at 150–160° and 15 mm for 30 hr and then at 180–190° and 20 mm for an additional 12 hr. The theoretical amount of water was collected in a cold trap in the system. The oily product was decanted and distilled to give 277.1 g (90%) of material which had bp 175–177° (2.0 mm); n^{27}D 1.4901.

Anal. Calcd for $C_{23}H_{38}$: C, 88.11; H, 11.89. Found: C, 87.73; H, 12.22.

6-Methyl-6-phenylhexadecane (1a).—Hydrogenation of 6-methyl-6-phenyl-7(8)-hexadecene at 70° and 1140 psig of hydrogen over 10% palladium-on-charcoal catalyst gave 90% of **1a**: bp 210.5° (11 mm); n^{25}D 1.4833.

Reaction of 2-Chloro-2-phenylheptane with Decylmagnesium Bromide.—2-Chloro-2-phenylheptane was prepared by saturating 2-phenyl-2(1)-heptene with hydrogen chloride gas at −45° and removing excess hydrogen chloride by purging with dry nitrogen. Alternately, 2-phenyl-2-heptanol in Skellysolve F was saturated at −40° with hydrogen chloride gas, the water separated, the solution dried over calcium chloride, and the solvent removed under vacuum. In either case, the water-white product was used without further purification.

Decylmagnesium bromide was prepared from 26.8 g (1.10 g-atoms) of magnesium metal and 283 g (1.28 mol) of 1-bromodecane in 460 ml of dry ether. When the preparation was complete, 400 ml of dry *n*-hexane was added and the solvent distilled until 650 ml of distillate had been collected and the pot temperature was 70–75°. This temperature was maintained while a solution of 229.8 g of 2-chloro-2-phenylheptane (from 1.09 mol of 2-phenyl-2-heptanol) in 200 ml of dry hexane was added dropwise to the reaction mixture during the course of 1 hr. The mixture was stirred an additional hour at 65–70° and then allowed to cool to room temperature. The mixture was worked up in the conventional manner to obtain, after filtration, a solid and a liquid product. The solid was recrystallized from ethanol to obtain 6,7-dimethyl-6,7-diphenyldodecane (**2**): mp 84–105°; nmr, ratio of aliphatic to aromatic protons, 2.8:1. The compound decomposed smoothly during attempted distillation or gas chromatography to give a 1:1 mixture of 2-phenylheptane and 2-phenyl-2(1)-heptene.

Anal. Calcd for $C_{26}H_{38}$: C, 89.08; H, 10.92. Found: C, 88.85; H, 11.14.

The original liquid product, having the composition shown in Table I, was distilled to obtain 104.3 g (30%) of pure **1a**; the physical constants and analytical data are shown in Table II. The infrared spectrum, nmr spectrum, and gas chromatography retention time of the 6-methyl-6-phenylhexadecane prepared in this manner were identical with those of the material prepared by reduction of 6-methyl-6-phenyl-7(8)-hexadecene. Fom the lower boiling fractions of the distillation was isolated by distillation 2-phenylheptane: bp 102° (11 mm); n^{25}D 1.4852; [lit.[13] bp 61–64° (1 mm), n^{20}D 1.4860].

(9) *Cf.* R. Palland and J.-M. Pleau, *C. R. Acad. Sci., Ser. C*, **265**, 316 (1967).

(10) Melting points were taken on a Reichert hot-stage melting point apparatus and are corrected. Molecular weights were determined by mass spectrometry. Nuclear magnetic resonance spectra were recorded with the Varian A-60 nmr spectrometer using tetramethylsilane as internal standard and carbon tetrachloride as solvent.

(11) W. C. Davies, R. S. Dixon, and W. J. Jones, *J. Chem. Soc.*, 468, (1930).

(12) A. C. Cope, C. M. Hoffman, C. Wyckoff, and E. Hardenbergh, *J. Amer. Chem. Soc.*, **63**, 3452 (1941).

(13) F. Asinger, G. Geiseler, and W. Beetz, *Ber.*, **92**, 755 (1959).

Anal. Calcd for $C_{13}H_{20}$: C, 88.56; H, 11.44; mol wt, 176. Found: C, 88.42; H, 11.32; mol wt, 176.

The reaction was repeated in refluxing ether and tetrahydrofuran (THF), giving the results shown in Table I; in addition, dimer **2** was isolated in 14 and 17% yield, respectively.

Reaction of 2-Chloro-2-phenyloctane with Octylmagnesium Bromide.—The reaction of 381.6 g of 2-chloro-2-phenyloctane (from 1.8 mol of 2-phenyl-2-octanol) and 2.2 mol of octylmagnesium bromide in 600 ml of *n*-hexane was carried out as described above for the reaction of 2-chloro-2-phenylheptane with decylmagnesium bromide in hexane. A total of 173.6 g of 7-methyl-7-phenylpentadecane (**1b**) was obtained by fractional distillation; physical properties and analytical data are shown in Table II.

Fractional distillation of the lower boiling products of the reaction afforded 4.2 g (1.2%) of crude 2-phenyl-2(1)-octene,[11] bp 114–120° (10 mm), $n^{25}D$ 1.5169, and 65.5 g (19%) of 2-phenyloctane,[11] bp 113–114° (10 mm), $n^{25}D$ 1.4838.

Anal. Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65; mol wt, 190. Found: C, 88.25; H, 11.79; mol wt, 190.

In addition to the above products, 114 g of solid, bp >130° (0.08 mm), was obtained in the reaction; it was not characterized, but was assumed to be predominantly 7,8-dimethyl-7,8-diphenyltetradecane by analogy to the product obtained from the reactions with 2-chloro-2-phenylheptane.

Reaction of 2-Chloro-2-phenylhepane with *n*-Butylmagnesium Bromide.—An ethereal solution of *n*-butylmagnesium bromide was prepared from 5.6 g (0.23 g-atom) of magnesium metal and 34.3 g (0.25 mol) of 1-bromobutane in 80 ml of dry ether. To this solution, maintained at 45–50°, was added dropwise a solution of 2-chloro-2-phenylheptane (from 0.21 mol of 2-phenyl-2-heptanol) in 60 ml of *n*-heptane. The mixture then was stirred at 45–50° for 1 hr. During the preparation of the Grignard reagent, a total of 30 ml of gas was evolved; during the addition of the 2-chloro-2-phenylheptane and the 1-hr reflux period, a total of 514 ml (0.023 mol) of gas was evolved. Mass spectrometric analysis of the collected gas revealed the presence of 43% of 1-butene and 34% of butane, and about 5.4% each of hydrogen, ethylene, propane and ether, and 1.8% of ethane (calculated on an air-free basis). The reaction mixture then was allowed to cool while a stream of dry carbon dioxide gas was bubbled in overnight. The mixture then was hydrolyzed and the acid product isolated. The infrared spectrum of the acid, 1.0 g, was identical with that of *n*-valeric acid; no aromatic impurity could be detected (estimated limit of detection, 5%).

The neutral organic portion of the product mixture was fractionally distilled to obtain 6.2 g of material, bp 101–133° (10 mm), shown by gas chromatography to contain 4.8 g (0.026 mol) of 2-phenylheptane and 1.5 g (0.009 mol) of 2-phenyl-2(1)-heptene, and 8.1 g (17%) of 5-methyl-5-phenyldecane (**1c**). The physical constants and analytical data for the *tert*-alkylbenzene are recorded in Table II.

During the distillation of the 5-methyl-5-phenyldecane there also was collected a total of 6.4 g (25 wt %) of a mixture of 2-phenylheptane and 2-phenyl-2(1)-heptene, formed by thermal cleavage of **2**.

Reaction of 1,4-Bis(1-chloro-1-methylpentyl)benzene with Butylmagnesium Bromide.—The following procedure is typical of that used for the preparation of the disubstituted *tert*-alkylbenzenes listed in Table III. A slurry of 320.9 g (1.16 mol) of 1,4-bis(1-hydroxy-1-methylpentyl)benzene in 410 g of *n*-heptane was saturated with hydrogen chloride gas at −20°. Water was separated and the clear, homogeneous organic layer was neutralized with 1 l. of cold 5% sodium bicarbonate solution, and then washed with 800 ml of cold water before drying over magnesium sulfate. This *n*-heptane solution of 1,4-bis(1-chloro-1-methylpentyl)benzene was used as such for subsequent reaction.

Butylmagnesium bromide was prepared from 75.3 g (3.1 g-atoms) of magnesium metal and 466 g (3.4 mol) of 1-bromobutane in 220 ml of ether. *n*-Heptane, 450 ml, then was added and the solvent distilled up to a pot temperature of 102°. The mixture was cooled to 40° and the *n*-heptane solution of 1,4-bis(1-chloro-1-methylpentyl)benzene added dropwise during 1.5 hr. The reaction mixture was stirred at 40–45° for an additional 2 hr, then allowed to cool to room temperature and stand overnight.

The mixture was worked up in the conventional manner and distilled to obtain 139.0 g of material, bp 110–130° (0.1 mm), and 94.7 g (23%) of 1,4-bis(1-butyl-1-methylpentyl)benzene, bp 135–136° (0.1 mm); a center cut, 45.5 g (11%), had the physical properties and analysis shown in Table III. Gas chromatograms of the center cut indicated less than 1 area % impurity. The nmr spectrum showed a complex of peaks at τ 8.28–9.32 (42 aliphatic protons) and a singlet at τ 3.00 (4 aromatic protons).

The 110–130° (0.1 mm) fraction from the reaction could not be separated cleanly into individual constituents by fractional distillation or by preparative scale gas chromatography. The nmr spectra of individual fractions suggested the presence of 1-(1-butyl-1-methylpentyl)-4-(1-methylpentyl)benzene and a mixture of isomeric 1-(1-butyl-1-methylpentyl)-4-(1-methylpentenyl)-benzenes, ratio 2.6:1 (vpc). The material was recombined and hydrogenated over 10% palladium on charcoal at 60 psig. The product was distilled to give 101.1 g (29%) of 1-(1-butyl-1-methylpentyl)-4-(1-methylpentyl)benzene. The analytical data are given in Table III: nmr τ 8.73–9.28 (m), and 8.50 (unresolved) (total of 33, aliphatic), 7.46 (pentet, 1, benzylic), and 2.95 (q, 4, aromatic).

The nmr spectra of the remaining dialkylbenzenes listed in Table III were identical with those cited above except for relative peak areas; in each case, the proton ratios agreed with the assigned structure. The infrared spectra of the compounds listed in Table III were essentially identical and exhibited bands at 3000–2850 (vs), 1520 (m), 1470 (s,) 1415 (w), 1380 (m), 1015 (n–w), 830 (s), and 720–730 cm^{-1} (m). Presence of bands at 830 and 1015 cm^{-1} and absence of absorption at 708, 790 and 890 cm^{-1} due to meta substitution confirmed the para orientation of the dialkylbenzenes.

Registry No.—**1a,** 26279-03-8; **1b,** 26279-04-9; **1c,** 26279-05-0; **2,** 26279-13-0; 1,4-bis(1-hydroxy-1-methylheptyl)benzene, 26279-14-1; 1,4-bis(1-hydroxy-1-methylpentyl)benzene, 26279-15-2; ethyl 2-cyano-3-methyl-3-phenyloctanoate, 26279-16-3; 3-methyl-3-phenyloctanenitrile, 26279-17-4; 6-methyl-6-phenyl-8-hexadecanone, 26279-18-5; 6-methyl-6-phenyl-8-hexadecanol, 26279-19-6; 6-methyl-6-phenyl-7(8)-hexadecene, 26279-20-9; 2-phenyl-2(1)-octene, 5698-49-7.

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